Laser-Induced Fluorescence Spectroscopy for Analysis of Cultural Goods

Subjects: Art

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With the rapid scientific and technological changes that occur every day, a new kind of necessity, for real-time, rapid, and accurate detection methods, preferably also non- or minimally invasive and non-destructive, has emerged. One such method is laser-induced fluorescence spectroscopy (LIF), applied in various fields of activity, ranging from industry and biochemistry to medicine and even heritage sciences. Fluorescence-based spectroscopic methods have all of the above-mentioned characteristics, and their functionality has been proven in many studies.

Keywords: laser-induced fluorescence spectroscopy ; hybrid techniques ; heritage sciences

1. Laser-Induced Fluorescence Spectroscopy (LIF) in Heritage Sciences

Most organic materials observed in art and archaeology and some inorganic ones have fluorescence properties, making them suitable for LIF studies. A search was conducted throughout several multidisciplinary databases (Clarivate WoS, Elsevier, Springer, and Wiley) using combinations of the following key-words: “laser-induced fluorescence spectroscopy” and “art”, “archaeology”, “paintings”, “organic binders”, “pigments”, “ceramics”, “graffiti”, “consolidants”, “adhesives”, “glue”, “bacteria”, “fungi”, “icons”, “mortar”, “bricks”, “marble”, “mural painting”, “secco”, and “fresco”, all of them related to materials identifiable through fluorescence spectroscopy or to the major object types. The returned results from the Elsevier, Springer, and Wiley databases showed that most LIF studies focus on the study of bacteria (~18%), followed by organic binders (~15%), adhesives (~13%), and pigments (~10.5%). WoS database results were related to studies on pigments (>25%) and art, in general (~18%), followed by bacteria (~14%). In both cases, less attention had been given to graffiti (<0.2%), secco (<0.35%), consolidants (<0.6%), marble (<1.20%), bricks (<1.35%), mural painting (<1.55%), and fresco (<1.70%).

Pigments are amongst the most encountered materials in the studied literature, along with polymers, waxes, resins, adhesives, organic binders, oils, and stones in the form of either laboratory mock-ups or real objects [1][2][3]. Some of the LIF studies were also focused on the analysis of natural and synthetic pigments, and towards identifying mural painting pigments [4][5][6][7], followed by an increase in studies oriented and contemporary artworks [8] and materials [9].

LIDAR applications, which allow the remote characterization of surfaces, were also an important part of LIF studies at the beginning of 2000, for the characterization of stone monuments and building façades, and the biological attack on such objects [10]. LIDAR studies were performed for the differentiation between green alga and cyanobacteria, based on the potential of LIF to highlight the presence phycobilin, a component found in cyanobacteria [11][12][13][14]. Another study was focused on the use of essential oils to remove cyanobacteria from walls, and proved that lavender and thyme essential oils were the most efficient in destroying phototrophic biofilms, without inducing alterations on the painted surface [15].

LIF capabilities were tested for determining specific spectral fingerprints of various rock types [14][16][17], for aiding the restoration processes. Enhanced results were obtained when LIF data were processed using multivariate techniques [10][13].

The investigation of organic media in paintings, including casein, egg yolk, and egg white, and animal tissues adhesives, along with the degradations associated with their natural or artificial aging was investigated through LIF-based studies ([18][19][20][21][22]).

Other types of materials, including consolidants [20], polymers [23] and textiles [24] were also studied, but to a lesser extent. Few articles have have been found in the scientific literature regarding these materials. Colao et al. [20] investigated vinylic or acrylic resins with multiple wavelengths for LIF, of with the best differentiation between the analyzed consolidants was obtained using a 266 nm wavelength. Di Lazzaro et al. [24] also used a 266 nm-laser to investigate stains and inscriptions on a famous copy of the Shroud of Turin, the Arquata shroud, indicating the high influence of cellulose on all the analyzed areas, along with degradation patterns of the cellulose fibers. By comparing the LIF spectra of the shroud with those collected from a sample of 400-years old naturally aged cellulose.

The majority of experiments involved the use of lasers emitting in the UV region, predominantly the 266 and 355 nm wavelengths, followed by the 248 nm wavelength, and, to a lesser degree, lasers in the visible-domain (442, 532 nm).

2. From Single to Hybrid Techniques

The recent technological advances have allowed the miniaturization of optics and electronics, thus promoting the design and creation of hybrid systems, by merging 2 or more techniques into a single equipment. For example, the combination of LIF with LIBS was tested using a nanosecond pulsed Nd:YAG laser [25][26], with pulse energies ranging from 2 to 20 mJ. Such systems were applied for the study of pigments, archaeological objects, or metal [27][28]. Another combination was that of LIF with Raman spectroscopy, tested for applications in the automotive and aeronautical industries, specifically flame combustion modeling [29][30], but there is no mentioning of such systems being used in heritage sciences. Starting from the proficient combination of Raman with LIBS [31][32][33][34][35], extended versions have been created, involving LIBS, Raman and LIF. Such types of hybrid systems have already been reported in severalstudies [36][37][38][39][40][41][42].

3. Enhancing LIF Analytical Capacity

One of the drawbacks in LIF is that compound identification is not always straightforward, many fluorophores have overlapping emission domains, which makes it difficult to identify them. Therefore, in cases when fluorophores identification is not a simple process, several authors have tried to find new ways to improve this process in the fluorescence spectra and resolve the overlapping broadband emission coming from different fluorophores.

A possible approach is to use time-resolved measurements. Time-resolved laser-induced fluorescence (TR-LIF) differs from conventional fluorescence intensity measurements by the fact that the emission detection occurs after the excitation has occurred, while for the fluorescence intensity measurements, excitation and emission occur at the same time. TR-LIF has been chosen by multiple authors, because it offers information beyond the possibilities of standard fluorescence intensity measurements, that is it can give information about the excited state dynamics and of fluorophores, and can overcome the shortcomings of conventional fluorescence intensity measurements [8][43]. Although not all investigated materials showed a usable signal, by selecting proper TR-LIF delay times and gate windows, Marinelli and collaborators [8][43] have been able to obtain the specific signal of several natural and synthetic binders and some commercial paints.

LIF results can be post-processed by applying chemometric methods, which help find hidden patterns within mixt signals. Many LIF studies involved principal component analysis (PCA), an unsupervised classification method which reduces the dimensionality of a large dataset and computes a new coordinate system, based on the entry data, in which the coordinates are known as principal components (PCs). PCA has proven useful for creating thematic maps, to point out vulnerable areas on the surface of the cathedral and baptistry of Parma, in Italy, to to analyze the different spectral shape and identify the separate contributions of bacterial and fungal strains, pigment classification, or to enhance the differential determination of individual fluorophores in mixtures of organic pigments in binders. Multivariate analysis has proven useful for the classification of different classes of binders, and also for differentiation between fresh and aged binding media.

4. Future

Given that LIF efficiency is greatly enhanced when coupled with multivariate data analysis methods and that hybrid techniques which incorporate LIF are continuously being developed and tested in both laboratory studies and field experiments, thus proving an ongoing interest for non-invasive, real-time investigation methods and set-ups, LIF appears to remain useful in the field of cultural heritage in the future. Possible areas that need to be further developed include historical documents and textiles, new ways of biocleaning, and even traceability of rocks, pigments or archaeological findings.

References

1. Miyoshi, T. Fluorescence from resins for oil painting under N2 laser excitation. Jpn. J. Appl. Phys. 1990, 29, 1727–1728.

2. Borgia, I.; Fantoni, R.; Flamini, C.; Di Palma, T.M.; Guidoni, A.G.; Mele, A. Luminescence from pigments and resins for oil paintings induced by laser excitation. Appl. Surf. Sci. 1998, 127–129, 95–100.
3. Castillejo, M.; Martín, M.; Oujja, M.; Silva, D.; Torres, R.; Domingo, C.; Garcia-Ramos, J.; Sanchez-Cortes, S. Spectroscopic analysis of pigments and binding media of polychromes by the combination of optical laser-based and vibrational techniques. Appl. Spectrosc. 2001, 55, 992–998.
4. Raimondi, V.; Andreotti, A.; Colombini, M.P.; Cucci, C.; Cuzman, O.; Galeotti, M.; Lognoli, D.; Palombi, L.; Picollo, M.; Tiano, P. Test measurements on a secco white-lead containing model samples to assess the effects of exposure to low-fluence UV laser radiation. Appl. Surf. Sci. 2015, 337, 45–57.
5. Ortiz, R.; Ortiz, P.; Colao, F.; Fantoni, R.; Gómez-Morón, M.; Vázquez, M. Laser spectroscopy and imaging applications for the study of cultural heritage murals. Constr. Build. Mater. 2015, 98, 35–43.
6. Almaviva, S.; Fantoni, R.; Colao, F.; Puiu, A.; Bisconti, F.; Nicolai, V.F.; Romani, M.; Cascioli, S.; Bellagamba, S. LIF/Raman/XRF non-invasive microanalysis of frescoes from St. Alexander catacombs in Rome. Spectrochim. Acta-Part A Mol. Biomol. Spectrosc. 2018, 201, 207–215.
7. Martínez-Hernández, A.; Oujja, M.; Sanz, M.; Carrasco, E.; Detalle, V.; Castillejo, M. Analysis of heritage stones and model wall paintings by pulsed laser excitation of Raman, laser-induced fluorescence and laser-induced breakdown spectroscopy signals with a hybrid system. J. Cult. Herit. 2018, 32, 1–8.
8. Marinelli, M.; Pasqualucci, A.; Romani, M.; Verona-Rinati, G. Time resolved laser induced fluorescence for characterization of binders in contemporary artworks. J. Cult. Heritage 2017, 23, 98–105.
9. Caneve, L.; Colao, F.; Del Franco, M.; Palucci, A.; Pistilli, M.; Spizzichino, V. Multispectral imaging system based on laser-induced fluorescence for security applications. In Proceedings of the Proc. SPIE 9995, Optics and Photonics for Counterterrorism, Crime Fighting, and Defence XII, Edinburgh, UK, 26–29 September 2016; p. 999509.
10. Weibring, P.; Edner, H.; Svanberg, S. Versatile mobile lidar system for environmental monitoring. Appl. Opt. 2003, 42, 3583–3594.
11. Cecchi, G.; Pantani, L.; Raimondi, V.; Tomaselli, L.; Lamenti, G.; Tiano, P.; Chiari, R. Fluorescence lidar technique for the remote sensing of stone monuments. J. Cult. Heritage 2000, 1, 29–36.
12. Lognoli, D.; Lamenti, G.; Pantani, L.; Tirelli, D.; Tiano, P.; Tomaselli, L. Detection and characterization of biodeteriogens on stone cultural heritage by fluorescence lidar. Appl. Opt. 2002, 41, 1780–1787.
13. Hällström, J.; Barup, K.; Grönlund, R.; Johansson, A.; Svanberg, S.; Palombi, L.; Lognoli, D.; Raimondi, V.; Cecchi, G.; Conti, C. Documentation of soiled and biodeteriorated facades: A case study on the Coliseum, Rome, using hyperspectral imaging fluorescence lidars. J. Cult. Heritage 2009, 10, 106–115.
14. Grönlund, R.; Svanberg, S.; Hällström, J.; Barup, K.; Cecchi, G.; Raimondi, V.; Lognoli, D.; Palombi, L. Laser-induced fluorescence imaging for studies of cultural heritage. In O3A: Optics for Arts, Architecture, and Archaeology; Society of Photo Optical: Bellingham, WA, USA, 2007; p. 66180P.
15. Bruno, L.; Rugnini, L.; Spizzichino, V.; Caneve, L.; Canini, A.; Ellwood, N.T.W. Biodeterioration of Roman hypogea: The case study of the Catacombs of SS. Marcellino and Pietro (Rome, Italy). Ann. Microbiol. 2019, 69, 1023–1032.
16. Pantani, L.; Cecchi, G.; Lognoli, D.; Mochi, I.; Raimondi, V.; Tirelli, D.; Trambusti, M.; Valmori, G.; Weibring, P.K.A.; Edner, H.; et al. Lithotypes characterization with a fluorescence lidar imaging system using a multi-wavelength excitation source. In Proceedings of the Remote Sensing for Environmental Monitoring, GIS Applications, and Geology II, Barcelona, Spain, 9–11 September 2003; pp. 151–159.
17. Giancristofaro, C.; D'Amato, R.; Caneve, L.; Pilloni, L.; Rinaldi, A.; Persia, F. Performance of nanocomposites for conservation of artistic stones. AIP Conf. Proc. 2014, 1603, 86.
18. Nevin, A.; Cather, S.; Anglos, D.; Fotakis, C. Laser-induced fluorescence analysis of protein-binding media, in the conservation of artworks. In Proceedings of the Lasers in the Conservation of Artworks: LACONA VI Proceedings, Vienna, Austria, 21–25 September 2005; Springer: Berlin, Germany, 2007; pp. 399–406.
19. Nevin, A.; Cather, S.; Anglos, D.; Fotakis, C. Analysis of protein-based binding media found in paintings using laser induced fluorescence spectroscopy. Anal. Chim. Acta 2006, 573–574, 341–346.
20. Colao, F.; Fantoni, R.; Caneve, L.; Fiorani, L.; Dell'Erba, R.; Fassina, V. Diagnostica superficiale non invasiva mediante fluorescenza indotta da laser (LIF) sulle pitture murali di Giusto de' Menabuoi nel Battistero di Padova. In Da Guariento a Giusto de'Menabuoi: Studi, Ricerche e Restauri; Antiga: Crocetta del Montello (Treviso), Italy, 2012; pp. 85–99.
21. Fantoni, R.; Caneve, L.; Colao, F.; Fiorani, L.; Palucci, A.; Dell'Erba, R.; Fassina, V. Laser-induced fluorescence study of medieval frescoes by Giusto de' Menabuoi. J. Cult. Heritage 2013, 14, S59–S65.
22. Anglos, D.; Georgiou, S.; Fotakis, C. Lasers in the analysis of cultural heritage materials. J. Nano Res. 2009, 8, 47–60.

23. Toja, F.; Nevin, A.; Comelli, D.; Levi, M.; Cubeddu, R.; Toniolo, L. Fluorescence and Fourier-transform infrared spectroscopy for the analysis of iconic Italian design lamps made of polymeric materials. Anal. Bioanal. Chem. 2011, 399, 2977–2986.

24. Di Lazzaro, P.; Guarneri, M.; Murra, D.; Spizzichino, V.; Danielis, A.; Mencattini, A.; Piraccini, V.; Missori, M. Noninvasive analyses of low-contrast images on ancient textiles: The case of the Shroud of Arquata. J. Cult. Heritage 2016, 17, 14–19.

25. Anglos, D.; Balas, C.; Fotakis, C. Laser spectroscopic and optical imaging techniques in chemical and structural diagnostics of painted artwork. Am. Lab. 1999, 31, 60–67.

26. Anglos, D. Laser-induced breakdown spectroscopy in art and archaeology. Appl. Spectrosc. 2001, 55, 186A–205A.

27. Telle, H.; Beddows, D.; Morris, G.; Samek, O. Sensitive and selective spectrochemical analysis of metallic samples: The combination of laser-induced breakdown spectroscopy and laser-induced fluorescence spectroscopy. Spectrochim. Acta-Part B At. Spectrosc. 2001, 56, 947–960.

28. Hilbk-Kortenbruck, F.; Noll, R.; Wintjens, P.; Falk, H.; Becker, C. Analysis of heavy metals in soils using laser-induced breakdown spectrometry combined with laser-induced fluorescence. Spectrochim. Acta-Part B At. Spectrosc. 2001, 56, 933–945.

29. Masri, A.R.; Dibble, R.W.; Barlow, R.S. The structure of turbulent nonpremixed flames revealed by Raman-Rayleigh-Lif measurements. Prog. Energy Combust. Sci. 1996, 22, 307–362.

30. Smith, N.S.A.; Bilger, R.W.; Carter, C.D.; Barlow, R.S.; Chen, J.Y. A Comparison of CMC and PDF Modelling Predictions with Experimental Nitric Oxide Lif/Raman Measurements in a Turbulent H2 Jet Flame. Combust. Sci. Technol. 1995, 105, 357–375.

31. Hoehse, M.; Mory, D.; Florek, S.; Weritz, F.; Gornushkin, I.; Panne, U. A combined laser-induced breakdown and Raman spectroscopy Echelle system for elemental and molecular microanalysis. Spectrochim. Acta-Part B At. Spectrosc. 2009, 64, 1219–1227.

32. Shameem, K.M.M.; Dhanada, V.S.; Unnikrishnan, V.K.; George, S.D.; Kartha, V.B.; Santhosh, C. A hyphenated echelle LIBS-Raman system for multi-purpose applications. Rev. Sci. Instruments 2018, 89, 073108.

33. Lin, Q.; Wang, S.; Guo, G.; Tian, Y.; Duan, Y. Novel laser induced breakdown spectroscopy–Raman instrumentation using a single pulsed laser and an echelle spectrometer. Instrum. Sci. Technol. 2018, 46, 163–174.

34. Shameem, K.M.; Dhanada, V.; Harikrishnan, S.; George, S.D.; Kartha, V.; Santhosh, C.; Unnikrishnan, V. Echelle LIBS-Raman system: A versatile tool for mineralogical and archaeological applications. Talanta 2020, 208, 120482.

35. Nevin, A.; Osticioli, I. Statistical analysis of laser-based spectroscopic data elucidates painting materials. SPIE Newsroom 2012.

36. Syvilay, D.; Bai, X.; Wilkie-Chancellier, N.; Texier, A.; Martinez, L.; Serfaty, S.; Detalle, V. Laser-induced emission, fluorescence and Raman hybrid setup: A versatile instrument to analyze materials from cultural heritage. Spectrochim. Acta-Part B At. Spectrosc. 2018, 140, 44–53.

37. Sharma, S.K.; Misra, A.K.; Lucey, P.G.; Lentz, R.C. A combined remote Raman and LIBS instrument for characterizing minerals with 532 nm laser excitation. Spectrochim. Acta-Part A Mol. Biomol. Spectrosc. 2009, 73, 468–476.

38. Syvilay, D. Evaluation of LIBS LIF Raman Spectroscopies to Analyze Materials from Cultural Heritage. Ph. D. Thesis, L'université De Cergy Pontoise, Paris, France, 2016. Available online: http://inis.iaea.org/search/search.aspx?orig_q=RN:52015148 (accessed on 25 January 2023).

39. Bai, X.; Oujja, M.; Sanz, M.; Lopez, M.; Dandolo, C.L.K.; Castillejo, M.; Detalle, V. Integrating LIBS LIF Raman into a single multi-spectroscopic mobile device for in situ cultural heritage analysis. In Proceedings of the SPIE 11058, Optics for Arts, Architecture, and Archaeology VII, Munich, Germany, 24–26 June 2019; p. 1105818.

40. Detalle, V.; Bai, X.; Bourguignon, E.; Menu, M.; Pallot-Frossard, I. LIBS-LIF-Raman: A new tool for the future E-RIHS. In Proceedings of the Proc. SPIE 10331, Optics for Arts, Architecture, and Archaeology VI, Munich, Germany, 28–29 June 2017; p. 103310N.

41. Gasda, P.; Acosta-Maeda, T.; Lucey, P.; Misra, A.; Sharma, S.; Taylor, G. A Compact Laser Induced Breakdown, Raman, and Fluorescence Spectroscopy Instrument for Mars Exploration. In Proceedings of the 45th Lunar and Planetary Science Conference, The Woodlands, TX, USA, 17–21 March 2014.

42. Dhanada, V.S.; George, S.D.; Kartha, V.B.; Chidangil, S.; Unnikrishnan, V.K. Hybrid LIBS-Raman-LIF systems for multi-modal spectroscopic applications: A topical review. Appl. Spectrosc. Rev. 2021, 56, 463–491.

43. Romani, M.; Marinelli, M.; Pasqualucci, A.; Verona-Rinati, G. A preliminary study of contemporary binders by Time Resolved Laser Induced Fluorescence (TR-LIF) spectroscopy: Characterization of the painting Nascita Della Forma by

Nato Frascà. In Proceedings of the Lasers in the Conservation of Artworks: LACONA XI Proceedings, Kraków, Poland, 20–23 September 2016; Nicolaus Copernicus University Press: Toruń, Poland, 2017; pp. 179–190.