Minimally-invasive analytical techniques for art and archaeological research

Marguerite Caycedo

*Literature thesis*

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Supervisors: Wim Kok and Freek Ariese

Cover photo: This past summer an elderly woman took it upon herself to “restore” a 19th century religious painting in a church near Zaragoza, Spain. The result is seen on the right.

Summary: Three analytical techniques were discussed in the context of research in the fields of art and archaeology. LIBS, OCT, and LA-ICP-MS are all minimally-invasive analysis techniques, which is important when working with fragile works of art or archaeological artefacts. These three techniques are becoming more popular in this field, and each of them has been found to have great potential for future research.
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LIBS, OCT and LA-ICP-MS

by

Marguerite Caycedo

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Supervisor:
Dhr. dr. Wim Kok
Dhr. dr. Freek Ariese
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Abbreviations and acronyms

AES    Atomic Emission Spectroscopy
FD-OCT Fourier Domain-Optical Coherence Tomography
FT    Fourier Transform
ICP    Inductively Coupled Plasma
ICP-AES Inductively Coupled Plasma-Atomic Emission Spectroscopy
INAA   Instrumental Neutron Activation Analysis
IR     Infrared
LA-ICP-MS Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry
LIBS   Laser Induced Breakdown Spectroscopy
LIF    Laser Induced Fluorescence
OCT    Optical Coherence Tomography
PIXE   Particle Induced X-Ray Emission
SD-OCT Spectral Domain-Optical Coherence Tomography
SEM-EDX Scanning Electron Microscope-Energy Dispersive X-Ray
SERS   Surface Enhanced Raman Spectroscopy
SLD    Superluminescent Diode
TD-OCT Time Domain-Optical Coherence Tomography
XRF    X-Ray Fluorescence
1. Introduction

The aim of art is to represent not the outward appearance of things but their inward significance – Aristotle.

It seems that ever since human beings have been able to hold something between their thumb and forefinger, they have created art in some form or other. As far back as Aristotle’s ancient Greece, if not before, we have been trying to understand the meaning of art, why it is made, and why it is important. Creating art is a universal human reaction, but is often very characteristic of a certain culture and religion. Art in combination with customs and traditions passed on from previous generations is then termed Cultural Heritage, and is important for a feeling of coherence and belonging in a group of people of the same cultural background. It remains difficult to explain exactly why people are compelled to create art, but Aristotle’s approach is a nice one and can certainly help to explain the continued fascination for art from the past to this day: it gives us an idea of how people have interpreted life through the ages, and can maybe help us understand it a little bit better ourselves.

That being said, Aristotle’s quote is also a nice way to introduce that other “inward significance” of art: its chemical composition. Tangible artefacts of Cultural Heritage (wall paintings, totem poles, religious masks, oil paintings, jewellery) all have unique chemistries that will have reacted differently to the inevitable consequences of time. The notion of restoring and conserving works of art to preserve them for future generations has been around since the 1800’s. Over the years it has become evident that to properly restore a work of art, knowledge of its chemical composition and the state of its decay is paramount. It is in this way that the fields of analytical chemistry and art history and archaeology come together. Analytical research can help to provide answers to the questions of where, when, and by whom a work of art or archaeological artefact was made, helping us to understand more about the history of the object and of course also for authentication purposes.

Analytical research in art and archaeology

The British Museum was the first to appoint a scientist specifically for the purpose of tending to works of art. This was in 1920 as the result of the First World War, as many works of art had been kept in unsuitable storage spaces underground for protection. However it was not until the 1960’s that analytical techniques began to be fully incorporated into art and archaeological research. Since then, a great number of institutes and laboratories have been opened specifically for this purpose, and a number of techniques have become ubiquitous to the field. X-Ray fluorescence (XRF) and particle induced X-Ray emission (PIXE) are used often for elemental analysis and fingerprinting of objects, as is atomic absorption spectroscopy (AAS) and various forms of mass spectrometry (MS). For molecular specification UV-VIS, laser induced fluorescence (LIF), infrared (IR) and Raman spectroscopies are applied. These are just a few examples of the many analytical techniques that have been found to be useful in this field. It will depend strongly on the object being studied, its chemical composition, the state it is in, whether sampling is possible
or not, and the information desired, which technique is the most appropriate, and this should be carefully determined beforehand.

When conducting chemical analytical research on art and archaeological artefacts, one of the most critical issues is that the least amount of damage is done to the work at hand. Sometimes it is possible to take small samples for analysis, but it is also sometimes the case that this is not possible at all. In any event, it is always the goal in art research to obtain the most information with the least amount of damage done to the object. In this paper, three techniques are discussed that are relatively new to the field of art and archaeological research. Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) make use of laser ablation sampling and are termed “micro-invasive” techniques, because the miniscule craters formed in the process are invisible to the naked eye but are nevertheless invasive to the object. Both techniques are elemental analysis techniques and are widely applicable. Optical Coherence Tomography (OCT) is an optical imaging technique that is purely non-invasive. The use of OCT carries the requirement that the sample be (semi-) transparent, and so this technique has a more limited applicability in this field.

The three techniques discussed here were chosen because they are relatively new to the field, having found a broader application only in the last decade or so. As will become clear during the course of this study, there is still room for development and improvement for each of these techniques, especially in the area of quantitative analysis, which is bound to be difficult for non-contact or micro-invasive techniques. It is also important to note that the questions surrounding an object of art can often not be answered by one analytical technique alone, and most often a variety of complementary techniques are combined with historical knowledge to reach a conclusion. The information then obtained is invaluable to our understanding of objects from the past, and for their preservation so that future generations can continue to learn from and be inspired by them.
2. Laser Induced Breakdown Spectroscopy

2.1 History and development
The most important aspect of Laser Induced Breakdown Spectroscopy (LIBS) is the laser, and so the history of the technique is tied to the development of the first lasers, beginning with Einstein’s ideas and developed into the first ruby lasers in the 1960’s. Runge et al. performed the first spectral analysis by LIBS in 1964, but in these early systems the laser was used only for ablation and excitation was induced by an electric arc. The technique really started to gain popularity in the 1980’s when lasers were improved and more sensitive CCD detectors were developed, as well as intensified CCD detectors for time-gated detection.

2.2 Theory and technique
Laser Induced Breakdown Spectroscopy is based on the technique of breaking down or “ablating” a very small amount of sample with the help of a laser. Simply put, a pulsed laser is focused through a focusing lens onto the sample surface (in the case of solids and liquids), irradiating it for a few nanoseconds (typically) and causing ablation of the irradiated material into a plasma that contains the elemental information of the sample. This elemental information exists in the form of ions, atoms, free electrons and molecular fragments, which have been vaporized by the laser pulse. Within the few nanoseconds of the pulse, its energy sustains the high temperature plasma and causes the fragmented particles to become excited and consequently to emit electromagnetic radiation. An optical fiber or lens system can then collect the light emitted from the plasma and transfer it to the spectrograph.

Figure 1 shows a simple LIBS setup, featuring the laser source, focusing mirror, optical fibers leading to the spectrograph, detector, and the computer screen.

Figure 1. Schematic diagram of a simple LIBS system. (a) laser source and cooler; (b) pulsed laser head; (c) mirror; (d) focusing lens; (e) excitation chamber; (f) sample; (g) collecting optics; (h) optical fiber; (i) detector trigger signal; (j) wavelength selector; (k) detector array; (l) microcomputer.

The nature of the ablation process requires the spectrograph to contain an ICCD detector for the possibility of time-gated detection. When the laser pulse first reaches the sample, it will initially heat the electrons at the surface of the sample. The very hot ones evaporate immediately, and the others heat the sample through collisions with the sample atoms. What follows is a melting of the irradiated surface, followed by an explosion-like evaporation to form the plasma, which will contain the elemental information in the form of molecules, clusters and ions. However right after the laser reaches the sample, there is not a real
plasma but only a high-density electron cloud giving off a signal. This will result in a very broad and un-informative spectrum. A gated detector will enable one to begin recording a spectrum about 1 µs after the of the laser pulse reaches the sample, when emission lines from the elements in the sample will be visible.\cite{5,7} A gated ICCD detector can also be useful in blocking out stray light in between laser pulses.

The ablated material will typically be on the order of 100 ng to a few µg, leaving a small crater on the surface of solid samples that is invisible to the naked eye.\cite{4} This is a very valuable characteristic of LIBS, making it attractive for a wide range of purposes, among them of course art and archaeological research.

An important distinguishing factor of LIBS is that the same laser source is used to ablate AND excite the sample.\cite{4} In regular LIBS this is done even within the same ns order pulse. A LIBS spectrum can thus be obtained within a second or less, which is another one of its great advantages. A double pulse technique can also be used in which a first pulse ablates the sample to form the plasma, and the second one excites the particles inside the plasma for emission. This dual-pulse technique has been observed to enhance emission signals and improve signal to noise ratios, though the reasons for this phenomenon are not entirely clear.\cite{8}

2.3 A closer look at the ablation process and important parameters

There are various factors that will have an effect on the ablation process of solid samples (which is most likely what one will be dealing with when doing art research), and it is worth taking a closer look at these parameters and the effect they can have.

First of all the laser is an important variable parameter. When analysing solid samples it is absolutely necessary to use a pulsed laser instead of a continuous wave. Continuous irradiation of the sample could cause serious damage, especially to fragile works of art. Furthermore the irradiated sample could start to melt and heat areas around it, changing the composition of the analysed area.\cite{7} One would have to use much lower intensities of irradiation with continuous wave lasers, which would not cause the same explosion-like evaporation process so effective for ablation.

Pulses of about 5 ns are most often used for LIBS, as this is short enough to allow the use of a laser intensity that is strong enough to cause ablation.\cite{7} Reducing the pulse length to the order of picoseconds or femtoseconds will also reduce the dispersion of heat by collisions between the high-energy electrons on the surface and the atoms of the sample. This will result in less melting of the irradiated region (before ablation) and consequently there will be less fractionation possible in the liquid phase, and a shallower crater is formed.\cite{7}

The wavelength of the laser is another parameter that is quite critical for LIBS analysis, as this will have an effect on the level of absorption and scattering of the sample. A high absorption of the laser beam will mean that a much thinner sample layer is removed upon ablation, thus increasing the depth resolution.\cite{9} In any case it is clear that different matrices will react differently to ablation and to irradiation with a laser of a particular wavelength, and
it is always important to take this into account and adjust all of the experimental parameters accordingly.\textsuperscript{[10]}

\section*{2.4 Other aspects of LIBS}

\subsection*{2.4.1 Quantitative analysis}

As a qualitative technique for the determination of elemental information, LIBS has proven to be a very valuable tool. Acquiring quantitative information however is somewhat more problematic. Theoretically, the peak intensity in the resulting spectrum can relate to the amount of elemental species in the vaporized plume and consequently to the concentration of the element in the ablated sample material.\textsuperscript{[11]} However in practice quantitative analysis is more complicated as calibration with reference materials is necessary and inhomogeneities in the sample can be problematic.\textsuperscript{[5]}

Colao et al. did a quantitative study on medieval glazed pottery samples, which present a number of difficulties. First of all, distinguishing exactly between the numerous layers of pigments and glazes is difficult, especially since some elements are abundant in different layers of glaze of which the thickness is unknown. Inhomogeneities in the sample can also cause problems. In this case a SEM measurement made it clear that the glaze was not distributed equally over the sample, and was thicker in some places than others and also included air bubbles. This was partially solved by making use of calibration lines and averaging data from different ablation points on the sample.\textsuperscript{[6]}

Violeta Lazic et al. tried to overcome difficulties in the quantitative analysis of ancient Mediterranean marbles, by using calibration standards of CaCO$_3$. This proved to be difficult however as the spectra of these standards and of the analysed material were not very similar, especially as far as emission intensities and plasma parameters were concerned. This can be attributed to the fact that the calibration samples were quite different in chemical and physical composition from the natural marbles, a factor which is critical for achieving similar sample ablation and emission and getting accurate quantitative results.\textsuperscript{[12]} It was therefore necessary to introduce a number of corrections regarding the temperature of the plasma, the electron density and the ablation rate, parameters which can have a large effect on emission intensities. These corrections were applied in the form of calculations for the deviations in the aforementioned parameters.\textsuperscript{[13]}

Various other studies have been done to obtain quantitative information from LIBS analysis.\textsuperscript{[12],[14],[15]} It remains however a much less straightforward tool than the qualitative aspect of LIBS.

\subsection*{2.4.2 Depth profiling}

Depth profiling of various material layers is another valuable application for LIBS. It can be achieved simply by applying multiple laser pulses at the same spot and recording spectra for each pulse. A small layer of pigment, paint, glaze, etc., will be ablated with each pulse, leaving the material underneath exposed to be analysed with the next.\textsuperscript{[5],[11]} Paint and varnish layers are typically about 5 to 50 µm thick, and on average about 0.5 to 2 µm is ablated with each pulse. This technique can be used to analyse the different layers of paintings, glazed
pottery, polychrome artworks, marble and metal objects. For restoration purposes this information can be essential, as knowledge of the composition of the artwork and the occurrence of different layers of materials is important for implementing the correct restoration procedure.

Figure 2. LIBS spectrum of a Bronze Age plaster sample from Thebes. Inset: first (a) and second (b) pulse LIBS spectra indicating weak emission of Fe in the first and increase of silicon emission in the second.

2.5 LIBS in combination with other techniques
Since the elemental information provided by LIBS is sometimes not sufficient to identify specific molecular compounds, studies have been done in which LIBS is combined with other spectroscopic techniques such as Raman microscopy, laser-induced fluorescence spectroscopy, time-of-flight mass spectrometry, amongst others. The combination of two complementary techniques can then provide a more complete analytical picture of the work being studied.

Raman spectroscopy provides molecular information on a sample by recording the energy difference between the incident light from a laser beam and the inelastically scattered light from the sample. Similarly to LIBS, it does not require sample preparation, it is highly sensitive (especially in resonance mode), and it has a high spatial resolution due to the possibility of laser focusing. It has proven to be a valuable tool for identifying the molecular properties of various types of art, especially pigments and paint dyes. The combined forces of Raman and LIBS can thus provide complimentary information and confirm the data provided by each one. Burgio et al. combined Raman and LIBS for the identification of pigments in 19th century paintings from Greece and France. Two separate systems for the two techniques were used in this case, where the information from each was combined with art historical knowledge of pigment dating to identify a wide range of pigments as well as confirm a tentative dating of the works.
More recently, setups that combine Raman and LIBS in the same system have been developed.\cite{26,27} In these, the same laser source is used for both Raman and LIBS analysis; for Raman a lower intensity pulse is applied and the scattered light is recorded with a spectrograph and ICCD detector, and for LIBS a higher intensity pulse is applied to form a plasma plume of ablated material. The ICCD detector is essential, as stated earlier, for allowing time-gated detection, especially of the LIBS analysis, as the broad background signal from the large electron density directly after the laser pulse must be filtered out. It is also valuable in filtering out a luminescence signal during the Raman measurement by applying time-resolved Raman analysis.\cite{27} Osticioli et al. used a combined Raman-LIBS setup to perform analyses on a mural painting, a piece of a decorative tile, and a bronze head.\cite{27}

Laser Induced Fluorescence is another molecular spectroscopic technique that is being used more and more frequently in combination with LIBS.\cite{9,11} In LIF, a monochromatic laser source is used to excite the sample, after which it will emit a characteristic radiation which is collected by a spectrograph. The emitted radiation may be characteristic of a certain compound, or it can be used to study the ageing and condition of varnishes.\cite{9} The use of lasers instead of regular lamp-based fluorescence is preferable in this context as lasers are more spatially precise and can be used in the pulsed form to achieve resolution in time. LIF can usually not be used for specific identification purposes of unknown substances, because of the occurrence of multiple fluorophores and the similarity of the fluorescence spectrum of many substances. It can therefore only be used in specific cases where the emitted fluorescence is very characteristic, or in the case of studying differences over time due to ageing or pollution.\cite{9} The combination of LIBS and LIF is ideal due to their similarities in experimental setup and the complimentary analysis that they provide, providing a much more complete analysis of a work of art than either one would separately.

In 2009, Osticioli et al. even proposed a system in which LIBS, Raman and LIF are combined in one instrument and uses a single pulsed laser source.\cite{28}
2.6 Application to art and archaeological research

All of the aspects of LIBS that make it attractive for other fields of research make it a valuable tool for art and archaeological research as well. The micro-destructive nature, analysis speed, the ability for in-situ analysis, and the fact that it does not require direct contact with the sample are all characteristics of a technique that would work well in this field. Especially over the last ten years, LIBS has been applied to a very wide variety of case studies for the elemental analysis of works of art. As stated earlier, quantitative analysis can still be problematic, and in most cases LIBS is used mainly qualitatively.

The first instance of LIBS being used for art historical analytical research was in 1972, when John Asmus was granted the task of cleaning Venetian marble statues by using a laser to ablate the black crusts that had accumulated over the years. In this first case the main goal was cleaning the statues through laser ablation of the unwanted top layer, which is still applied for the cleaning of a wide range of archaeological artifacts. LIBS adds an extra dimension to laser cleaning as it can provide on-line elemental analysis and feedback during the cleaning process. Lazic et al. used this technique for monitoring the cleaning of black crusts off of marble statues, caused by environmental pollution. Researchers have become aware of the fact that over-cleaning a work of art, especially artifacts like sculptures and buildings that are constantly exposed to the elements, can be extremely harmful and cause further and faster deterioration. In this case LIBS was used to monitor the elemental composition of the ablated material, so that it would be immediately obvious when the undesired top layer had been sufficiently removed and to avoid removal of a layer from the actual artwork.

Castillejo et al. applied LIBS to monitor the laser cleaning process of 14th century Spanish polychromes on wood, as well as to gain elemental insight into the pigments used. By applying a number of pulses after each other at the same position, it was possible to distinguish between the polluted top layer and various layers underneath, combining the elemental information provided by LIBS with the knowledge of the pigments commonly used in that region in the 14th century. Lopez et al. did a similar depth profiling study of 17th century Baroque Spanish wood polychromes with LIBS.
P. Pouli et al. used LIBS for a depth profile study of the protective layers of historic metal objects (acrylic resin varnishes, cellulose nitrate coatings and waxes), in which knowledge of the material composition and of the state that these protective layers are in is again stressed as extremely important for effective restoration and preservation. In this study the thickness of the coating layers was measured by determining how many laser pulses were applied before reaching the metal artifact (essentially a type of on-line monitoring as well).

As a qualitative tool, LIBS has furthermore been used to characterize the elemental composition of metal artifacts from a Romanian monastery, Roman ceramics, 19th century daguerreotypes, Roman ceramics, cinematic film, oil paintings, to name just a few specific studies. Lazic et al. even did a LIBS study on archaeological artifacts under water, in which they made use of dual pulse laser excitation and two lenses to achieve tighter focusing and narrower and more intense spectral emission.

It is important to note that many studies combine the qualitative, quantitative and depth-profiling aspects of LIBS, and it is sometimes combined with other techniques as well to give a more complete analytical picture.

2.7 Advantages and disadvantages / comparison to other techniques
As can be deduced from the many applications of LIBS to art and archaeological research that have been illustrated, it has many advantages for analysis in this field. One of the biggest issues in the analysis of artworks is the taking of samples, which is often either not allowed or not possible. A big advantage of LIBS is then that sampling is minimal and a sample does not have to be removed from the object prior to analysis. The amount of material ablated in a single pulse is tiny (20-200 ng), and the crater left behind is invisible to the naked eye. The instrumentation is straightforward and allows for in-situ analysis and the possibility of portable instruments, for example for the analysis of buildings and outdoor statues or artworks that cannot be moved.

However the very small samples that are analysed in a single pulse can also be viewed as a disadvantage, as inhomogeneities in the sample could have a disproportionate effect on the analysis results. It can therefore be necessary to take multiple spectra in different positions to be sure of accurate data. Luckily the analysis speed of LIBS is extremely fast so this can

Figure 4. LIBS spectra taken after the indicated number of successive laser pulses as performed by Castillejo et al. on a green area of the polychrome. Increase of relative intensity of Cu lines (indicating the use of a Cu based green pigment compound) compared to Ca, Mg and Al lines reveals the removal of the contaminant top layer.
be done easily. Another disadvantage is that one has to be careful with the shockwave produced by the laser during LIBS. Already flaky or cracked paint layers could be damaged further due to the impact of the laser, for example.\[21\]

Finally, elemental analysis might not be sufficient for an artefact in which the same element is included in different substances and layers throughout the sample. Combined analysis of LIBS with other molecular analysis techniques such as Raman or Laser Induced Fluorescence spectroscopy could be very helpful in these instances.

LIBS compares favourably to a number of the more conventional elemental analysis techniques used in art research. SEM-EDX is ideal for the mapping of the elemental composition of objects, however it cannot be performed in-situ and a sample must be removed from the object prior to analysis.\[5\] XRF is a good and established technique that is non-destructive and is able to achieve multi-elemental analysis and a good spectral resolution, similar to LIBS. It can also be used portably. However it is not useful for elements lighter than sodium and its depth resolution is not ideal (10-50 µm).\[5\] PIXE is also a good multi-elemental analysis technique with a very high resolution and sensitivity, and quantitative analysis is relatively simple. Analysis can be performed in-situ, but only once the object has been transported to the specialized facility where the ion accelerator is located.\[40\] LA-ICP-MS, which will be discussed in detail later on in this paper, has extremely low LOD’s and makes use of the same laser-ablation sampling technique as LIBS, however this technique also does not allow for transportable instrumentation.

It should be noted that it might depend on the objects being studied which technique will be the most suitable. In reality it will also depend on which instrumentation is the most accessible for the researchers at that time, as not every lab or museum will have all of these different machines to choose from.

3. Optical Coherence Tomography

3.1 History and development
The basics of Optical Coherence Tomography (OCT) begin with Michelson interferometry, which was developed by Albert Abraham Michelson around 1881 to study the speed and traveling properties of light.\[41\] Figure 4 shows the basic setup for a Michelson interferometer. A beam of light is split in two and directed towards two mirrors, which reflect the beams back towards the beam splitter where they are recombined and directed towards the detector. The detected interference pattern then depends on the distance and orientation of the mirrors to the beam splitter.
All forms of interferometry are based on the Michelson interferometer, including OCT, which was first developed by David Huang et al. at MIT and published in Science in 1991. It was developed primarily for non-invasive imaging in biological systems, most notably the eyes. The extreme vulnerability of the materials for which analysis by OCT was first developed, makes it ideal for the examination of works of art as well.

3.2 Theory and technique

OCT is a type of low-coherence interferometry that enables one to obtain cross-sectional views of semi-transparent objects non-invasively. Tomography is the principle of obtaining two-dimensional data from the internal structure of a three-dimensional object. In short: a beam from the optical source is split into a reference beam, which is reflected by a reference mirror, and an object beam, which will reflect light from the sample. Both reflected beams are then combined again and the interference signal is directed towards the detector. Low-coherence length light must be used as this determines the axial (depth) resolution of the system. The lateral resolution depends on the width of the light beam inside the sample, and thus on the imaging optics of the system. As stated above, the technique was first proposed by Huang et al. in 1991 when they combined low-coherence reflectometry with tomographic imaging to measure the internal structures of biological systems. Figure 5 shows a diagram of this setup. The light from a super-luminescent diode (SLD) is split by the beam splitter and directed towards a sample arm and a reference mirror arm. The reference mirror can be scanned longitudinally, and the amplitude of the interferometric signal from the recombined sample and reference beams is detected simultaneously. However a signal is only detected when the two beams interfere constructively. This is especially true because of the low-coherence light, for which the signal will be dissipated quickly in the event that there is no constructive interference, and which allows high-resolution detection of the position of the sample reflection sites.

A series of longitudinal scans (of the reference mirror) are performed to obtain the data for the creation of a two-dimensional image of a layer within the sample. This is done by scanning the depth across a lateral beam axis, and thus acquiring information on a cross

Figure 5. Michelson interferometer.
sectional slice of the sample. This is called an A-scan and can effectively be seen as the intensity of the back-scattered light as a function of depth. It is important to note that these intensities can never be interpreted as purely quantitative, because the semi-opaque materials will absorb and scatter some of the light as it passes each way through the sample. Finally, a three-dimensional image can then be constructed by combining the cross sections of orthogonal lateral depth scans.\cite{41}

![Figure 6. Schematic of the OCT system described by Huang et al. in 1991. \cite{42}](image)

As stated above, the use of a low-coherence light source is of great importance for obtaining a good depth resolution. This has to do with the relationship between the line width (spread of $\lambda$ components) ($\Delta\lambda$) and the coherence length ($l_c$), which is described by:

\[ L_c = \frac{4\ln 2}{\pi} \times (\frac{\lambda^2}{\Delta\lambda}) \]

From this equation it is clear that the larger the line width of the source, the smaller the coherence length, and consequently the better the depth resolution that can be achieved.\cite{44} For this reason the most commonly used light sources for OCT are superluminescent diodes, which have a large wavelength bandwidth and still quite a high power output.\cite{41} They are generally used in the NIR region where absorption of the objects under analysis will be lowest.\cite{45}

This first type of OCT is referred to as Time Domain OCT, in which the optical path difference between the reference and sample beams is physically adjusted by moving the reference mirror to obtain a depth reflectivity profile (the time delay of the light scattered off the internal structures of the sample is measured indirectly through the interferometer).\cite{44,46} This technique is quite slow due to the mechanical limitations of having to move the reference mirror arm. A more recent type of OCT termed Spectral Domain or Fourier Domain OCT does not require this moving reference arm for depth scanning and is much faster. In spectral domain OCT the reference mirror is kept in place, and the interference between reference and sample beams is detected as a spectrum (spectral interferogram) with the help of a CCD camera, which is then Fourier Transformed into an axial scan.\cite{41} This method is faster (by about 100 fold) for two reasons. The advantage is not only in the fact that no moving parts are required, but also in that only a single exposure is necessary to collect the back-scattered light from each layer in the sample and create an axial A-scan.\cite{46}
Targowski et al. were able to obtain 10-15 cross-sectional images per second, and predict that with the advent of better and faster computers, on-line monitoring with OCT will be possible. Real-time monitoring of the laser ablation cleaning of varnish layers off of paintings is named specifically as an application for which OCT could have advantages over LIBS, which is often used for this purpose (see LIBS section). OCT will be preferable when working with NIR lasers, as a plasma is usually not generated at these wavelengths, and when only a partial removal of the varnish layer is desired. LIBS only provides information on whether the varnish-paint layer interface has been reached, and thus when all of the varnish has been removed. OCT on the other hand, when the ability to provide real-time cross-sectional images is reached, will be able to show how much of the varnish layer remains, therefore providing more specific information.\[^{46}\]

Besides the advantage of improved acquisition speed for spectral domain OCT, a very significant increase in signal to noise ratio has been demonstrated as well.\[^{47}\] This mainly has to do with the multi-array detectors used in SD-OCT, compared with single-element detectors for TD-OCT. The spectral dispersion of each detected wavelength means shot noise at one wavelength will not necessarily affect the signal to noise ratio at all other wavelengths. For a single-element detector used in TD-OCT, each wavelength is encoded as a unique frequency on the same detector and the shot noise at one wavelength can effect the entire tomogram.

### 3.3 Other aspects of OCT

The depth to which the light beam can penetrate into the sample is highly dependent on the degree of absorption and scattering of the sample and thus also on the wavelength of the light.\[^{41}\],[^48] However due to the many different pigments and substances present in works of art, selecting an optimum analysis wavelength is difficult in this application.\[^{41}\] Most commonly used sources are used with wavelengths between 600 and 2000 nm where the main components in medical diagnostics and pigments have low absorption.\[^{44}\] Longer wavelengths tend to improve the penetration depth, however this will have a negative effect on the depth resolution which is of course extremely undesirable, unless the optical bandwidth of the source is adjusted as well.\[^{49}\]

Another difficulty that one can run into with OCT experiments is the appearance of speckle noise from highly scattering samples. Light from the source will be scattered off of different microscopic points in the sample, and will still have the same coherence (and so can be detected) but will have slight differences in path length and phase.\[^{41}\] The OCT images will then contain patterns of bright and dark “speckles”, where the back scattered light interferes constructively and destructively, which can be particularly problematic when trying to detect very thin layers. Various methods of post-processing or changes to the hardware of the system can be employed to reduce the interference of speckle patterns in the OCT tomograms.\[^{41}\]
3.4 Applications to art and archaeological research

The nature of the OCT technique, and one of its greatest limitations, requires that the material under analysis be transparent or semi-transparent. The most valuable application of OCT is therefore the analysis of paintings and varnish layers, not an unimportant one of course. When an object is suitable for analysis by OCT, the method has a number of advantages. Most importantly it is a non-contact, non-invasive method, though some care must be taken with regard to the laser power to avoid unnecessary damage. High axial and spatial resolutions are possible when the appropriate light source and imaging optics are selected. Furthermore it is a technique with high precision and sensitivity. [50]

Figure 7. Example of the multi-layered varnish over the paint layer: (a) microphotograph, UV excited fluorescence; (b) OCT tomogram. Arrows point to interfaces between consecutive varnish layers. [45]

As stated previously, OCT is extremely suitable for the study of protective varnish layers, and consequently this is the area in which it has been most applied. It was first used for this purpose in 2004 by Targowski et al. to study the glaze coating on porcelain and a 19th century oil painting. [50] In the same study they also used OCT to visualize the effects on the surface of a painting upon exposure to an extremely humid environment. Bajraszewski et al. performed a similar humidity study of the surface of an oil painting with OCT the following year. [51] Other early applications of OCT for art and archaeological research include a 2004 study by Yang et al. of ancient jade artefacts that were typically buried together with their deceased owners. [52] After centuries of being underground, the interiors of the jade objects undergo a whitening process, giving them a distinct look. Unfortunately, forgers have found ways of artificially whitening jade objects to make it seem as if they were centuries old. On the surface it is very difficult to tell the difference between a fake and an authentic ancient jade object. Yang et al. proposed the use of OCT to obtain cross-sections of, and study the
internal structures of ancient jades and forgeries for comparison. They found the internal structures to be quite different and this method to be successful in identifying a forged object.

Since then, a number of other studies have been published on the examination of varnish layers. Gorszynska et al. used spectral domain OCT for the determination of the thickness of a varnish layer on an easel painting, finding similar results to those from the microscopic image of the cross-section of a sample taken from the painting. In 2005 Liang et al. used en-face OCT for the study of easel paintings. In this case a system was used in which the en-face or lateral scanning was the fast component and the depth scanning is performed at a slower rate. This enabled the examination of the entire painting layer by layer, in which comparison with the visible top layer of the painting is fast and simple. In this way, depth profiles were successfully obtained from varnish on glass samples and from a fifty-year-old test painting, from which the researchers were able to determine various layers of varnish, as well as under drawings. The following year Targowski et al. used spectral domain OCT for the construction of three-dimensional maps of varnish layers on an easel painting, and in another study for tracking the deformation of a painting over time upon exposure to alternately humid and dry environments. Szkulmowska et al. used a longer central wavelength for the application of OCT to the examination of paint layers. Due to the absorption of the pigments in paints in the visible region, working with a longer wavelength (1.55 µm in this case) is bound to be more successful. Even so, distinguishing the paint layer and the paint-ground layer interface of the forty-seven paints analysed proved difficult. This was due to the high level of scattering and/or absorption, even at this wavelength (a comparative study was done with a 823 nm SLD and the results were even worse). Spectral domain OCT has also been used to generate en-face tomograms of gold punch work characteristic of Italian Renaissance paintings. Since gold is highly reflective in the NIR region, a very detailed image of the gold can be created, as no light will penetrate through the surface of the gold layer.

As mentioned earlier, preliminary studies have been done on the use of OCT for the monitoring of the laser-ablation cleaning of art works. This was first done by Góra et al. in 2006, using sample resins applied to fused silica plates to simulate the varnishes on paintings. OCT was found to be very useful in showing the depth and size of craters formed during ablation, as well as any deformations to the material underneath and around the ablation craters. Targowski et al. did a study on specially prepared substrates of oil paintings and cardboard supports covered in various varnishes, including one that was made according to an old varnish recipe. The experiment then proceeded by ablating a very small amount of material and consequently performing an OCT scan of the ablated area. This allowed for a very precise removal of the varnish layer, which would be very useful when working with fragile paintings and other objects for which the removal of a layer underneath the varnish could be disastrous. In another study by Targowski et al. mentioned earlier, the structural analysis of a painting and a stained glass sample by OCT was performed along with functional imaging of the laser ablation of the varnish layer of a painting. This was done by obtaining fifteen cross-sectional images per second that could be stored for further processing. This allowed the construction of video footage of the ablation process, and is
the closest thing to real-time imaging in art research reported to date. A recent article reported a new way of parallel processing data from spectral OCT tomograms to achieve much faster processing and the ability for real-time imaging.\textsuperscript{[61]} Though it is reported that the quality is not yet ideal, it is an indication that real-time imaging with OCT will most likely be available in the near future.

Finally, an interesting application of OCT which has come to light in recent years is for the examination of artists’ signatures and other forms of writings on paintings.\textsuperscript{[46],[60],[62]} The stratigraphy of paint and varnish layers can provide valuable information on the position of an artist’s signature, whether it lies on the same level as the top paint layer, or whether it has been painted on top of a varnish layer and covered with another layer of varnish, thus exposing a fake. UV-fluorescence spectroscopy will not be able to detect any inconsistencies if a fluorescent layer has been applied over the whole painting on top of the fake signature.\textsuperscript{[46]} An OCT tomogram on the other hand can reveal the situation of the signature, as seen in figure 7. This clearly shows that the signature has been applied on top of the original varnish layer, and can provide strong evidence that the person who made the painting was not the one who applied the signature.

\textbf{Figure 8.} Example of an OCT examination of a signature. In the OCT cross-sectional image, it becomes obvious that the signature has been applied on top of the original varnish layer, after which a new varnish layer has been applied on top. \textsuperscript{[62]}

It is important to note here that many of the studies with OCT to date were performed on specially prepared samples, and references are often made to future applications. It is obvious that a lot more research and development is necessary before this technique becomes widely implemented in the art and archaeological science fields.

\subsection*{3.5 Advantages and disadvantages / comparison to other techniques}

A great advantage of OCT is that it has the ability to characterize objects layer by layer, without actually having to remove any of them, making it a completely non-destructive technique. The resolution with which it can do this (defined as half the coherence length of the light) enables the distinction between very thin layers, such as layers of varnishes, glazes and paints.\textsuperscript{[57]} The ability to obtain three-dimensional images of works of art is also an important advantage. The great disadvantage however, is that a great number of materials
and works of art are not suitable for analysis by OCT because the material must be at least semi-transparent so that not all of the light is absorbed.

The most common technique for the imaging of paintings is of course NIR reflectography or IR photography, which can reveal under drawings of paintings because the overlying paint layers become transparent at infrared wavelengths. However this technique is not able to distinguish between different layers, or determine in which stratum the appeared under drawing is located. It is also not very useful for distinguishing different varnish or glaze layers as these are all transparent. The potential for OCT to become a household technique for the analysis of especially paintings, but also ceramics and other works of art that are covered with varnishes or glazes, is therefore enormous.

4. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

4.1 History and development
Mass spectrometry has been under development ever since J.J. Thompson discovered the electron in 1897 and consequently determined its mass to charge ratio. The idea of using Inductively Coupled Plasma as an ion source, and laser ablation sampling for this type of Mass-Spectrometry were only discovered in the 1980’s however.

4.2 Theory and technique
Mass spectrometry is one of the most widely used analytical techniques, and can be applied to a great variety of research fields. A range of different types of instruments (ion sources and mass analyzers) can be used to create the ideal instrument for the type of analyte being studied. What characterizes all mass spectrometers however is the excellent selectivity and limits of detection, as well as the speed of analysis. For a sample to be analyzed by Mass Spectrometry, gas phase ions of the analyte must be produced with the help of a so-called ion source, which should be selected for the specific sample under analysis. These ions are then transferred to the mass analyzer, where they are separated with respect to their mass-to-charge ratio. The abundance of each ion (each mass to charge ratio) is then detected and a spectrum is formed.

Inductively coupled plasma is an ionization source that is especially useful for measuring inorganic substances, making it ideal for the analysis of minerals, pigments and metals. In a traditional ICP-MS, the sample is introduced into the ICP torch as a solution spray. In the ICP, an argon plasma of between 8000 and 10000 K is sustained, and the sample “droplets” are transported into the plasma by a carrier gas, usually also argon. The very high temperature plasma will then vaporize, atomize and ionize the sample (typically into positive ions), after which the ions are pumped out of the plasma and into the mass analyzer.

Instead of using a nebulizer or another type of liquid based introduction method, Laser-Ablation ICP-MS makes use of the same sampling technique as LIBS: laser ablation of a miniscule amount of solid material. This technique allows direct sampling from a solid
artefact (work of art or archaeological find), and requires only that the sample surface be cleaned prior to analysis. The sample must generally be mounted into the ablation chamber, limiting the sample size, and after irradiation with the laser the ablated material is transferred directly into the ICP. In the section on LIBS the ablation process is discussed in detail. It is important to note that in this case, the laser is used only as a sampling method and the particles generated by the ablation are ionized only in the ICP torch.

Figure 1 shows a basic scheme for an LA-ICP-MS system.

![Basic scheme for an LA-ICP-MS system.](image)

Various parameters in an LA-ICP-MS can be adjusted to optimize the system for the analysis of your sample, and are important to consider when using this technique. The first important adjustable parameter concerns the laser and will have an effect on the size of the ablation crater formed and the amount of material ablated. This involves taking into account the energy of the laser beam and the type of material under analysis, as well as the number of pulses directed at each point of analysis. Nevertheless it is always difficult to determine exactly the amount of sample that has been ablated and the amount that is transferred and reaches the ICP chamber. For this reason quantitative analysis can be difficult and will require calibration curves and internal standards, which are discussed further on. Wagner et al. performed an extensive study on Corning archaeological reference glasses, which are often used as standards for the analysis of historical glasses. They determined the laser wavelength and the pulse length to have a very large effect on limits of detection of these glasses (three different wavelengths were compared), and also on the detected elemental signal, giving some quite deviating results.

Parameters of the ICP torch such as the power of the generator and the carrier gas flow rate can also be adjusted to obtain the strongest possible signal of the analyte elements. These adjustable parameters add to the sensitivity of the system and are part of what make LA-ICP-MS such a valuable tool for trace elemental analysis in works of art. In fact ICP-MS systems are extremely sensitive to a very broad range of elements in the periodic table, with detection
limits (in the parts per million to parts per trillion range) up to three orders of magnitude better than techniques such as ICP-Optical Emission Spectroscopy.\textsuperscript{[64],[69]}

4.3 Other aspects of LA-ICP-MS

4.3.1 Interferences

Due to its excellent sensitivity and limits of detection for many elements, LA-ICP-MS is often used in cultural heritage research for the analysis of trace elements in for example archaeological iron\textsuperscript{[66]}, limestone\textsuperscript{[69]}, and obsidian\textsuperscript{[70]}, to obtain information on how and where an artefact was made. One of the biggest problems that can be encountered in these instances is the interference of matrix effects from the sample. The extent of the interference will depend on the matrix itself, and can cause the occurrence of a signal that is either too high or too low for the actual amount of analyte present in the sample.\textsuperscript{[64]} This is of course particularly problematic for quantitative analysis, especially when working with external reference and calibration standards. Standard reference samples are used in most cases from NIST, but for some substances these do not exist or they will still differ from the analyte matrix. Also, for a group of artefacts of a similar nature, the matrix could turn out to be quite different, leading to deviating quantitative results even with the help of a reference standard. The use of an internal standard can be helpful in these cases to correct for differences in the matrix and also for differences between the reference and sample matrices.\textsuperscript{[71]}

Another type of interference that must be taken into account when doing LA-ICP-MS analysis is that of spectral interferences, otherwise known as isobaric interferences.\textsuperscript{[64]} This type of interference involves the overlapping of elemental peaks in the spectrum, which can be problematic in identifying the analyte of interest. These overlapping peaks may be the result of doubly charged ions, the formation of oxides during ionization, elemental combination, the formation of polyatomic ions, or it may result from elements present in the sample matrix.\textsuperscript{[64],[72]} To avoid these types of interferences it is necessary to carefully select the elements and isotopes to be analyzed.\textsuperscript{[68]} One could also increase the resolution of the MS system if this is a very big problem, however this will lead to a decrease in sensitivity and so it is not the most ideal solution.\textsuperscript{[64]}

4.3.2 Spatially resolved analysis

As with LIBS, LA-ICP-MS has the ability to perform spatially resolved analyses of artworks. Devos et al. used it for the spatially resolved analysis of archaeological iron (or rather the elemental impurities in the iron, which can provide provenance and production information).\textsuperscript{[66]} These samples included areas of corrosion or holes and even charcoal in some cases, which needed to be excluded during the analysis. This called first of all for the necessity of a solid sampling technique, so that the substances to be excluded would not be mixed with the “good” parts of iron that the authors were interested in (which is what would happen if the sample were to be liquefied). Secondly, the ability to choose exactly where the samples were taken and a resolution that was good enough for excluding the unwanted areas were requirements. LA-ICP-MS was therefore the method of choice in this case. Wagner et al. used LA-ICP-MS for the analysis of a 16\textsuperscript{th} century manuscript, in which an elemental profile distribution was made.\textsuperscript{[73]} This was done by directing the laser over a path of 2.5 mm,
which traversed a part of a letter on the manuscript page. In this way a distribution pattern of $^{57}\text{Fe}$ and $^{65}\text{Cu}$ (major components of historical iron gall inks) could be constructed. However it must be noted that while the spatial resolution component of LA-ICP-MS can be very helpful in some cases, bulk analysis of materials is more difficult, especially in combination with the difficulties with calibrations and standards. On the other hand, Resano et al. demonstrated that with the use of proper standards and calculations, it should be quite possible to perform bulk quantitative analysis with LA-ICP-MS, though the internal standard was determined by SEM-EDX. In any event, methods such as INAA and SEM-EDX can still compete with LA-ICP-MS due to these relative difficulties, despite the fact that the sensitivity of LA-ICP-MS is far superior.

4.4 LA-ICP-MS in combination with other techniques

The nature of an LA-ICP-MS system is such that it would be difficult to directly combine this type of analysis with another technique. However due to the difficulties with calibration methods often encountered, LA-ICP-MS is often performed next to another experimental technique. Also, when an internal standard is necessary, the concentration of the chosen element in the analyte must be known prior to analysis with LA-ICP-MS. A technique such as SEM-EDX can be used to determine major components in a sample (its detection sensitivity is much lower than that of LA-ICP-MS) and for the determination of concentrations for an internal standard. SEM can also be used prior to LA-ICP-MS analysis to gain information on the surface of the sample to be analyzed and determine ideal positions for sample ablation.

4.5 Application to art and archaeological research

As with LIBS and OCT, one of the biggest advantages of LA-ICP-MS for art and archaeological research is the fact that no complicated sample preparation or digestion is necessary prior to analysis. However, as opposed to LIBS analysis where the possibility of portable instruments exists and spectra can be taken directly off of a work of art, LA-ICP-MS requires that the sample fit inside an ablation chamber. This at times will require samples to be taken, or samples to be broken or cut into smaller pieces, making this a more destructive method to the artwork. However the technique itself is still only a “micro-destructive” technique (in the form of the ablation crater), and the sample will be available afterwards for further analysis by another technique if necessary.

Due to its excellent sensitivity and limits of detection for many elements, LA-ICP-MS is most often used for trace elemental analysis of works of art. Information on the trace elemental fingerprint can yield information on where or how something was made. It can also be used to group artefacts together that were made at a specific site or during a particular time. Green and Watling (2007) used LA-ICP-MS for the analysis of Australian aboriginal paintings. The traditional artists of the last century often included ochre in their works of art, which is a mixture of clay and a naturally occurring metal oxide (iron, silicon, aluminium, manganese), and which will be distinctive of a certain geological area. The trace elements present in the ochre can also be a distinguishing factor when determining provenances. Samples of ochre’s taken directly from nature, as well as samples from artworks, were analysed with LA-ICP-MS and subsequently subjected to statistical and “group” analysis by a
search/match compatibility index developed by the authors and also by principal component analysis. This proved to be a very successful and reproducible method in grouping samples from the same area and identifying the provenance of an unknown sample.

Insoll et al. similarly used LA-ICP-MS for the analysis of carnelian beads from India and Sub-Saharan Africa, to investigate whether a link could be made to a trade route between these areas.\[76\] Beads excavated at sites on both continents were inspected with LA-ICP-MS analysis and consequently subjected to cluster and principal component analysis to determine the extent to which their major and trace elements coincided. Standardization was difficult in this case due to the lack of carnelian standard reference material, and glass from NIST was used instead. A number of groups were identified, with some overlap between samples from India and regions of sub-Saharan Africa, however linking samples to specific excavation sites was difficult and it was concluded that more research would be needed for more definite statements.

The analysis of glass artefacts has also been found to be a valuable application for LA-ICP-MS. This is largely due to the fact that glass samples are generally quite homogeneous, and that there is a broad availability of matrix reference standards available.\[1\] Dussubieux et al. have done studies on African glass beads to look into ancient trade routes across the continent similar to Insoll et al. with carnelian.\[77\] Though major and minor trace elemental analysis was very successful using LA-ICP-MS and provided valuable information on the different glassmaking methods, it was difficult to establish clear distinctions such that definitive statements on provenances and trade routes of the beads could be made. Robertshaw et al. conducted a study of glass beads found in the Moroccan city of Al-Basra, and found six distinctly different types of beads (chemically speaking) for which they were able to draw

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1 A very recent article by Wagner et al. on often used Corning archaeological reference glasses (mentioned earlier when discussing the influence of the laser wavelength), however, came to the conclusion that a thorough re-evaluation of these reference glasses is necessary and that for some elements the reported values in the literature differ significantly from what they found.\[8\]
some connections to other ancient sites throughout Africa.\textsuperscript{[78]} Other examples of glass analysis by LA-ICP-MS are the determination of discriminating factors between glass artefacts from Egypt and Mesopotamia from the late Bronze age\textsuperscript{[79]}, and discriminating between locally made façon-de-Venise glass vessels from Antwerp from those that were imported from Venice in the 16\textsuperscript{th} and 17\textsuperscript{th} centuries.\textsuperscript{[80]} Both of these studies made use of fingerprint and rare earth elemental (REE) analysis to come to these conclusions. Schultheis et al. found lead isotope ratio analysis to be more successful than trace elemental grouping for the characterization of a collection of Art Nouveau glass samples by LA-ICP-MS.\textsuperscript{[81]}

![Figure 11](image)

\textbf{Figure 11.} Glass beads from Al-Basra (Morocco) were linked by Robertshaw et al. to other ancient sites in Africa.

Another type of archaeological artefacts for which LA-ICP-MS has been found particularly useful is pottery and ceramics. During a study for which the authors wanted to use LA-ICP-MS for distinguishing between organic and mineral paints, they discovered that not only was this possible but it was also possible to characterize different types of paints within these two subgroups.\textsuperscript{[82]} Neff included depth profiling measurements using LA-ICP-MS in his study on Mesoamerican plumbate pottery, in which it was found possible to distinguish between two sources of plumbate used by potters, which agreed with archaeological data obtained previously.\textsuperscript{[74]}

Furthermore, LA-ICP-MS studies have been conducted on the provenance establishment of limestone used in buildings of the ancient Mexican city of Teotihuacan,\textsuperscript{[69]} of obsidian artefacts from the Mediterranean and Near-East to look into trade routes in this region,\textsuperscript{[83]} and of ancient gold objects.\textsuperscript{[84]} Fingerprint lead isotope analysis has also been conducted on Roman coins to gain information on where and how they were made.\textsuperscript{[72]} A more recent study made use of LA-ICP-MS to determine arsenic concentrations in single strands of hair from 5000-year-old mummies from the Atacama Desert.\textsuperscript{[85]}

It is obvious that the list of applications for LA-ICP-MS is extensive and varied and will continue to grow in the future as the technique is perfected and the availability of standard reference materials is expanded.
4.6 Advantages and disadvantages / comparison to other techniques

Compared to LIBS and OCT, LA-ICP-MS would be termed the most destructive of the three. Analysis must be carried out in the lab and no portable devices have been developed to date. Also, smaller portable artefacts may still have to be broken or sampled to fit into the ablation chamber of the LA-ICP-MS system. However the technique is still itself only micro-destructive and after analysis with LA-ICP-MS samples may still be used for analysis with other methods or saved for follow up analysis.

As has been discussed, one of the biggest drawbacks is that quantitative analysis is difficult with laser ablation methods. The difficulty begins with the variations in the amount of sample ablated for each laser pulse and the amount of sample and analyte actually reaching the ICP. All of these issues can have an effect on the observed analyte signal. The other problem with this method is inhomogeneities in the sample, which will have a large influence for bulk analyses because of the spatially resolved sampling (which can also be an advantage, depending on the sample and the aims of the study). This would not be an issue when working with traditional ICP-MS where a much larger amount of sample would be used. Traditional ICP-MS is however a strictly destructive method so one would have to decide which is more important.

In the past, instrumental neutron activation analysis (INAA) has been the method of choice for analysing trace elements in works of art. In a study by James et al. in which a collection of ceramics and a collection of archaeological obsidian were analysed by both methods for comparison, it was found that LA-ICP-MS provided similar and accurate information to INAA after performing multivariate analysis of the results. LA-ICP-MS was found to be less precise because the internal standard was not able to totally correct for the variations in ablated sample mass with each laser pulse, however this did not seem to have a very negative effect for the multivariate analysis and the characterization of the samples for provenance groups. Advantages of LA-ICP-MS over INAA include a much faster analysis time, lower costs, and the ability to detect a much wider range of elements in smaller amounts. Also, samples could still be radioactive for quite some time after analysis with INAA, which could be a problem if an object is to be returned to a museum.

As stated earlier, SEM and SEM-EDX are often used in the same context as LA-ICP-MS in art research. Rather than being simply advantageous or disadvantageous, these techniques should be termed complementary. SEM-EDX is not suitable for trace elemental analysis, however it is crucial for determining major components in a sample and at times also for determining the concentration of an internal standard for LA-ICP-MS. It is however so that sample preparation for SEM analysis is more destructive and laborious than for LA-ICP-MS, and the analysis time is much slower. Similarly, XRF can also be used to detect more abundant elements in a sample, but this technique cannot determine between isotopes of the same element and is not appropriate for detecting light elements (atomic number smaller than 11 or so). It does however offer the possibility of portable instrumentation.
Three analytical techniques have been discussed with application to the fields of art and archaeological research. The importance of these techniques in this field lies in the fact that they are so-called non-invasive or minimally-invasive techniques and are thus suitable for the analysis of fragile and valuable objects of art.

LIBS is a simple elemental analysis technique that makes use of laser ablation sampling, giving it a good spatial resolution and the opportunity for portable and combined devices. OCT is a non-contact, non-invasive technique that allows for the investigation of the inner layers of paintings, ceramics and other objects that contain semi-transparent layers, as well as the construction of 3D images of these layers. LA-ICP-MS also makes use of laser ablation sampling and is very effective in conducting trace elemental analysis due to its excellent sensitivity. The biggest difficulties for LIBS and LA-ICP-MS have to do with quantitative analysis at this point, as better methods for quantifying the amount of sample removed during laser ablation sampling must be found. OCT is still in its very early stages of development as an analytical tool in this field, but the results obtained up to now are quite promising.

Furthermore, it has become clear that different types of techniques are suitable for different types of artworks or archaeological artefacts. Every technique is bound to have some limitations and will not be appropriate for the analysis of certain materials. It is therefore very important to evaluate what one is dealing with and the information that one wishes to obtain, before proceeding with the analysis. Most likely more than one technique will be necessary to obtain a complete picture of the chemical composition for the object being studied. This fact adds to the importance of non-invasive and non-destructive techniques: if a sample is taken, it is ideal if this one sample can be used for a number of different analyses, so that damage to the artwork remains at a minimum.

With the constant development of newer and better technology, the three techniques discussed here are bound to gain a lot of ground in the field of art and archaeological research in the future. Their simple sample preparation and fast analysis time add to their plus of being minimally-invasive techniques. Most important though, is the information that they will be able to provide us with in order to learn from and preserve our valuable cultural heritage.
References


[64]. E. de Hoffmann, V. Stroobant, *Mass Spectrometry: Principles and Applications*, John Wiley & Sons Ltd, West Sussex, UK, **2002**.


