



1.3. Chemical composition/structural characterisation using spectroscopic techniques

Spectroscopy is the study of any interaction of a substance with radiated energy as a function of its wavelength or frequency. Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency.

1.3.1. Fourier-transform infrared spectroscopy (FTIR)

Introduction to FTIR spectroscopy

Infrared radiation is that part of the electromagnetic spectrum between the visible and microwave regions. In simplest terms, spectroscopy is defined as the interaction of light (radiation) with matter. When infrared (IR) light is passed through a sample of an organic compound, some of the frequencies are absorbed, while other frequencies are transmitted through the sample without being absorbed. Molecules absorb IR radiation while undergoing a net change in dipole moment from the vibration or rotation between constituent atoms. When the electron density (charge distribution) of the two atoms is different, the fluctuations in dipole moment, from the vibration or rotation, produce an electric field that can interact with the electric field of the IR radiation, resulting in absorption of the IR radiation. If we plot absorbance or transmittance on the y-axis against frequency or wave number on the x-axis, the result is an infrared spectrum. An IR spectrum displays detector response



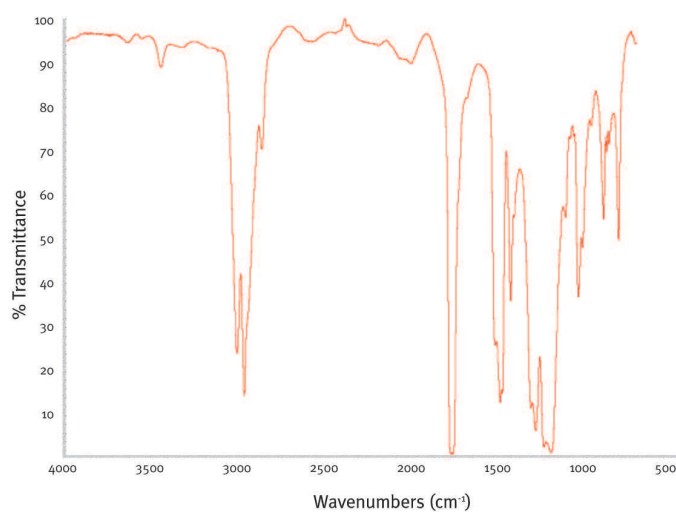


Figure 7. FTIR transmission spectrum for PMMA



Figure 8. FTIR microscope

as percentage transmittance (% T) and IR frequency in terms of wavenumber (reciprocal wavelength).

Historical development of IR spectroscopy meant that originally IR spectra were recorded by scanning a narrow band of IR radiation having intensity I_0 through the polymer sample and comparing the transmitted light intensity I with the incident light. Most modern IR spectrometers do not use the narrow band scanning, but instead the sample is exposed to broad band IR radiation and a beam-splitter and moving mirror produce two beams with path lengths that vary periodically to give interference patterns. The Fourier transform is a mathematical operation used in the data processing and the method is denominated as Fourier transform infrared spectroscopy (FTIR).

Within any molecule, a given functional group (a combination of atoms such as a carbonyl group or an amide group) is responsible for IR absorptions at or near the same frequency, regardless of the rest of the molecule. A large polymer molecule has a multitude of localised dipole moments and therefore produces a rich IR spectrum.

This spectrum can be used like a fingerprint and compared against a database of known spectra. FTIR spectroscopy has long been one of the mainstays in the analysis of organic compounds and is quite useful in both qualitative and quantitative analysis of polymeric materials. Identification of polymers is ideally suited to IR analysis, but has become somewhat more difficult with the many blends of polymers that now exist. The advantages of FTIR spectroscopy for plastics include: very small (or no) sample required; very speedy and accurate analysis; many commercial polymer spectra libraries available for comparison.

In order to produce good spectra it is necessary to choose the most appropriate technique for presenting the sample to the spectrometer. In transmission methods the beam passes through the sample. In reflection methods the changes in the IR beam as it is reflected by the sample is measured.

Although bench top FTIR spectrometers have been in use for decades, contemporary FTIR analyses couples a microscope to the spectrometer for the analysis of minute samples. This method is particularly relevant for the analysis of art objects where sampling is an issue (Figure 8).

The introduction of the diamond anvil cell in the 1960's allowed solid samples to be analysed via transmission methods. This is achieved by the production of a very thin film of the solid by clamping it between 2 diamond surfaces under pressure.

This method is very commonly used today for the analysis of plastics and rubbers. The minute sample is placed on the window of the diamond cell (Figure 9) and examined under the microscope. In



Figure 9. Sample preparation tools and diamond cell

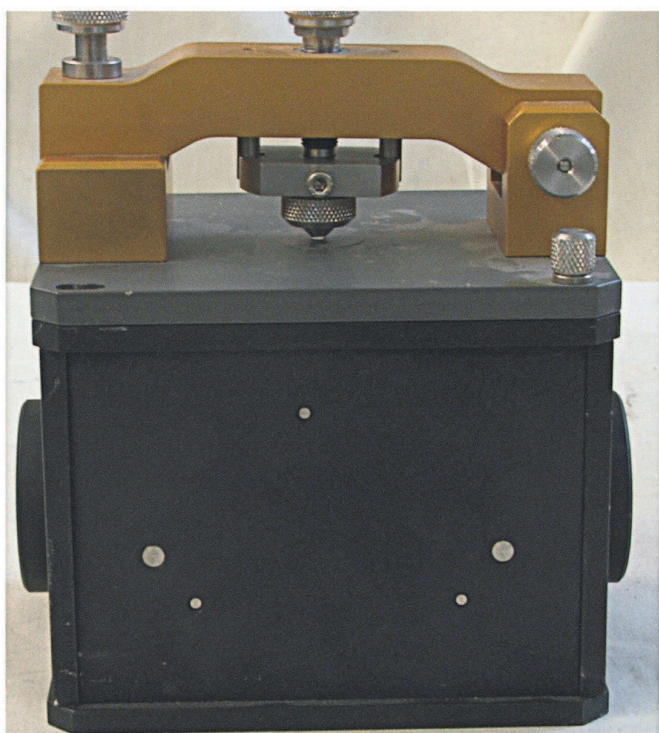


Figure 10. Golden Gate attachment for ATR measurements

this way different areas of the sample can be examined and spectra taken at each location.

Reflectance techniques such as attenuated total reflectance (ATR) enable materials to be examined directly in the solid. Previously ATR attachments such as the Golden Gate (Figure 10) were used in conjunction with a bench-top spectrometer were used for samples of materials such as foams and rubbers.

Current ATR attachments work well with plastics and depending on the size of the object, do not need any sample to be removed. If the object is small then the ATR accessory is put in contact with the surface of the object and the pressure increased until an acceptable spectrum is obtained.

Diffuse reflectance (DRIFTS) is another reflectance technique used in conjunction with a bench-top system in which the IR beam is diffusely reflected from the surface of a sample. The minute amount of sample required is collected by rubbing the object gently with silicon carbide paper.

FTIR was used by several partners to analyse the SamCo: Victoria and Albert Museum, The Getty Conservation Institute, Laboratoire du Centre de recherche et de restauration des musées de France (LC2RMF) and Rijksdienst voor het Cultureel Erfgoed (RCE).

LC2RMF describes briefly a practical example below: for each SamCo plastic micro-sample was removed with a scalpel. In order to be sure that the analysis was not contaminated the surface layer, to a depth of around a half mm, were removed with a scalpel. The samples were flattened between the windows of a diamond micro-compression (Spectra Tech, Tucson, AZ, USA, diamond surface 500 μm) and analysed using a transmitted infrared beam with a Perkin Elmer Spectrum 2000 instrument. The spectra collected were acquired at a resolution of 4 cm^{-1} in the mid IR (between 4000 and 400 cm^{-1}) and are the sum of 32 scans.

The interpretation of the results was achieved through comparison with commercial (Fluka and Perkin Elmer ATR polymer), and institutional database (libraries) and with the analysis of the signal based on a personal experience.

The analyst first uses a computerised search program that undertakes spectral comparison to find the best match and list these. The program provides a list of reference compounds that match the unknown spectrum most closely. The identification is done after the selection of the one that matches exactly or the best.

For the early plastics such as cellulose nitrate and formaldehyde based resins, commercial spectrum references are rarely available. Therefore, interpretation has been performed by reference to literature in scientific books and articles.



It is interesting to note that fillers, pigments or dyes have been rarely detected on the spectra, certainly because these are in low amount compared to the polymer.

Almost of the samples has been identified except for the black coloured samples where the infrared transmission failed. For dark coloured plastic analysis with an ATR accessory must be considered.

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1.3.2. Hand-held FTIR

The fragile and rare nature of heritage material requires minimum disturbance to the artefact, avoiding loss of key information and integrity, whilst gaining maximum information. There are a number of analytical techniques available to the conservation scientist; these include destructive, non-destructive and non-invasive techniques. Non-invasive techniques are preferred where available and applicable, requiring no sample removal and leaving the investigated area intact.

Commonplace techniques for organic materials analysis, readily accessible to museums and the heritage sector, usually rely on some degree of sampling, although the analysis may not cause any damage to the sample itself. Recent studies have investigated mid-infrared analysis outside of the sample compartment. The ability to identify a material on site without the need for sampling can provide museum professionals with a useful tool for successful collections management.

Experimental

A2 Technologies portable ATR-FTIR with a diamond/zinc selenide crystal, employing a scan range of 650-4000 cm^{-1} , wavenumber resolution of 4 cm^{-1} and scan accumulation of 4. All spectra acquired in absorbance mode.

Examples and results

Many of the most prominent sculptors active in post war USA Los Angeles became well known for utilising a vast array of new resins, paints, and plastics, all of which were being developed at that time for use in industries such as aerospace and automobile.

These artists also often adopted highly innovative fabrication processes to create seamless, bright, and pristine looking objects,



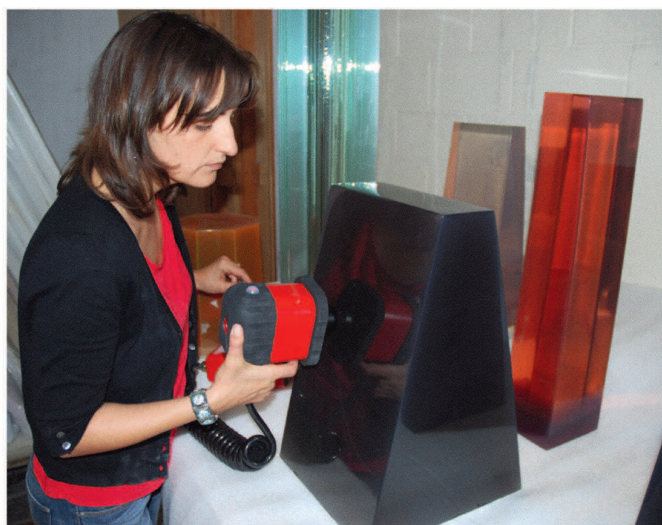


Figure 11. In situ analysis of a De Wain Valentine sculpture using portable ATR-FTIR

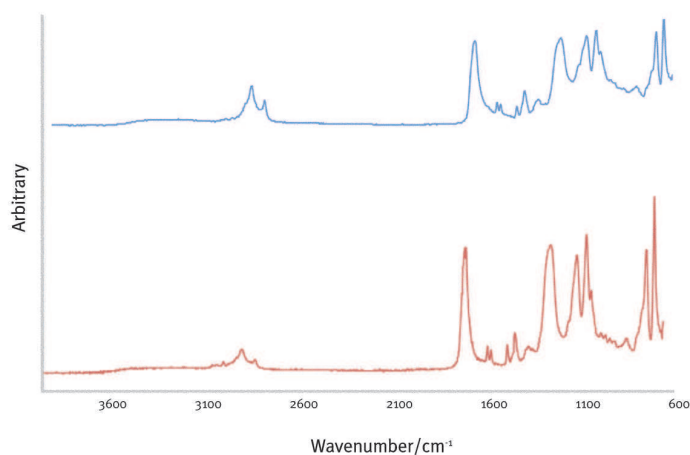


Figure 12. Offset absorbance spectra of the De Wain Valentine sculpture (lower) and an unsaturated polyester resin spectrum SamCo 64 (upper)



directly inspired by California culture and landscape. The sensuous colours and beautiful, pristine surfaces that were often painstakingly achieved by artists, such as Peter Alexander, Larry Bell, Billy Al Bengston, Robert Irwin, Craig Kauffman, John McCracken, Helen Pashgian, and De Wain Valentine, earned them the label “Finish Fetish” artists.

The nature of these pristine surfaces means that sampling for analysis is not possible, therefore technical examination of these artworks requires non-invasive methods. Figure 11 shows the onsite analysis of a De Wain Valentine sculpture using portable ATR-FTIR, with the corresponding spectra seen in Figure 12. The lower curve is that acquired on-site from the Valentine sculpture, with the upper spectrum relating to an unsaturated polyester resin sample SamCo 64.

Characteristic bands relating to unsaturated and saturated aliphatic vibrations $2959\text{--}2856\text{ cm}^{-1}$, ester vibrations at 1719 cm^{-1} , 1250 cm^{-1} and 1116 cm^{-1} , and aromatic moieties due to the presence of styrene and phthalic acid anhydride at 1600 cm^{-1} , 1451 cm^{-1} , 1492 cm^{-1} , 702 cm^{-1} and 741 cm^{-1} .

The spectra clearly illustrate the capabilities for onsite analysis and identification of polymers.

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1.3.3. Raman spectroscopy

Introduction

The Raman effect was discovered in 1928 by the Indian scientist Sir Chandrasekhara Venkata Raman and, for this achievement, he received the Nobel Prize for Physics in 1930.

When a molecule interacts with laser light three scattering processes may occur in a molecule. The incident light will be elastically scattered as Rayleigh scattering, or show either Stokes or anti-Stokes Raman scattering which is inelastic scattering. Rayleigh scattering has the same energy as the incident light and is the far most intense signal, whereas Raman scattering is very weak. Approximately one out of one hundred million incident photons give Raman scattering.

When photons collide with the electron cloud of a molecule, electrons are excited. The molecule absorbs some of the energy, resulting in an excited vibrational state, and the remaining energy is



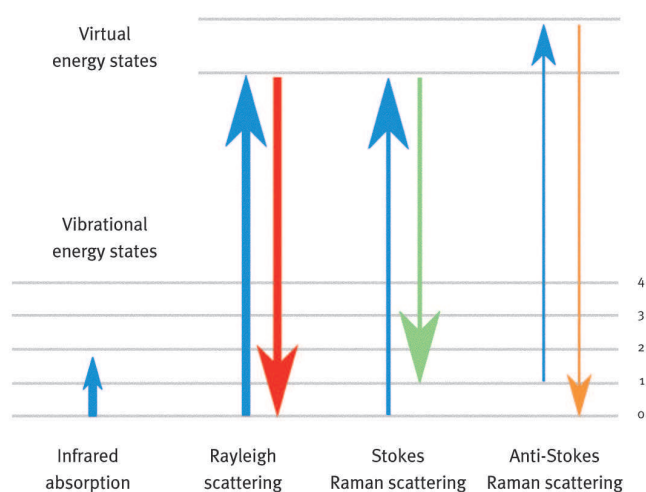


Figure 13. Schematic representation of Stokes Raman spectroscopy, Rayleigh and anti-Stokes Raman spectroscopy Scattering.

scattered as Stokes Raman scattering. Anti-Stokes Raman scattering occurs when electrons from a vibrational state are excited. At room temperature the population of molecules in a higher vibrational state is very low and therefore the anti-Stokes spectrum is less intense than the Stokes spectrum. Conventional Raman spectroscopy makes use of the Stokes spectrum (Figure 13).

A photon that impinges the molecule has an electrical field E , which is a set value depending on the initial laser wavelength. This oscillating electrical component can distort the electron cloud of the molecule and causes an electric dipole moment, μ . The amount of distortion of the electron cloud is called polarisability, α . The relation between these variables can be deduced from this formula:

$$\mu = \alpha E$$

The molecular polarisability measures the ease of displacement of electrons in a molecule by an electric field. Change in the molecular polarisability is required for a molecule to exhibit a Raman effect. The amount of the polarisability change will determine the Raman scattering intensity.

The energy lost by the photons in case of scattering is called the Raman shift (ΔE_r) and is defined in energy as:

$$\Delta E_r = E_i - E_s$$

E_i = energy incident photon

E_s = energy scattered photon

Raman shifts are commonly expressed in wavenumbers and then denoted as cm^{-1} . The Raman spectrum corresponds to the wavelength (or energy) dependence of the Raman scattered intensity at a given incident wavelength. Peaks in the Raman spectrum correspond to vibrational modes of the molecule, in a similar fashion as for an infrared absorption spectrum.

Experimental

Spectra were measured with a PerkinElmer Raman Spectrograph 400F combined with a Raman Micro 300 Raman microscope, equipped with a CCD detector and a diode laser operating at 785 nm with a maximum power of 96 mW.

Sampling size

Samples with a size of about 0.5 mm^2 are placed on a glass slide covered with aluminium foil.



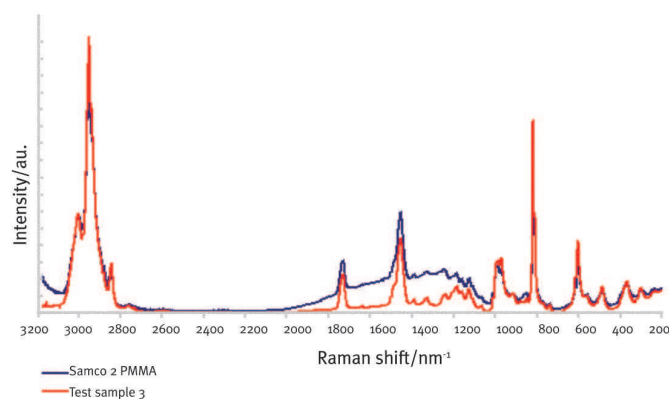


Figure 14. Raman spectrum test sample 3, laserpower 96 mW, 5 s x 50

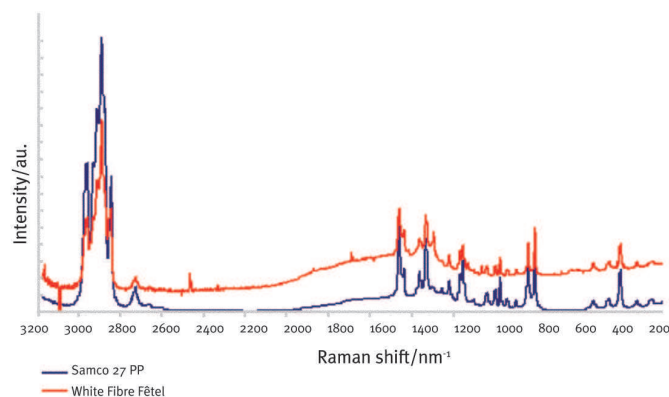


Figure 15. Raman spectrum white fibre Fête I, laserpower 96 mW, 10 s x 50

Examples and results

To build a reference library of Raman spectra for the identification of plastics, the Raman spectra of the standard references from the SamCo were recorded. The result is a spectrum database of 44 spectra. Using the library different test samples from the blind test could be identified, for example sample number 3 was analysed.

The spectrum of sample 3 (Figure 14) was used for an Euclidean search in the library, PMMA (SamCo no.2) gave the highest score. This is confirmed by visual comparisons of the two spectra as the sample spectrum shows great similarities with this reference. The spectrum shows specific Raman shifts at: 2950 cm^{-1} (CH_3 stretching), 1727 cm^{-1} ($\text{C}=\text{O}$ stretching), 1450 cm^{-1} ($-\text{CH}_3$ deformation), 810 cm^{-1} ($\text{C}-\text{C}$ stretching).

The reference database was also used for the identification of a white fibre from the wall tapestry “Fête I” (1971) by the artist Will Fruytier. The tapestry shows severe degradation at the front, the fibres are very brittle and powdery. The spectrum of the white fibre (Figure 15) was compared to the library and the highest score was for polypropylene. The spectrum shows specific Raman shifts at: 2882 cm^{-1} (CH_3 stretching), 1459 cm^{-1} ($-\text{CH}_2-$ scissor), 1359 cm^{-1} ($\text{C}-\text{H}$ deformation $\text{C}-\text{CH}_3$), 809 + 840 cm^{-1} doublet (specific for polypropylene).

Further reading

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Le Ru E. C and P. G. Etchegoin. 2009. Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Amsterdam, Elsevier.

Edwards H. G. M. and J. M. Chalmers. 2005. Raman Spectroscopy in Archeology and Art History, RSC Analytical Spectroscopy Monographs.

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1.3.4. Ultraviolet visible and near infrared spectroscopy (UV-Vis-NIR)

Introduction

For historical reasons, the majority of methodologies available in conservation science for the analysis and characterisation of plastic materials are borrowed from the field of industry, where non-invasive sampling is not an essential pre-requisite. As a consequence, even when artworks investigations are concerned, the most well established techniques used for plastic identification are based on sampling (FTIR, ATR-FTIR, Py-GCMS, etc.) and may be destructive or, at least, micro-destructive, (e.g. spot tests, heating tests, etc.) (Shashoua 2008). Conversely, in the museum context safeguarding the integrity of the objects and minimising the recourse to sampling are considered as paramount criteria in any conservation programme. In addition to the sampling considerations portability of the analytical instruments is of main importance. The inherent value of the artefacts, as well as the sheer size of some of the artefacts often prevents them from being transported to the analytical labs for analyses.

Although a number of different non-destructive methodologies are nowadays available for investigations on traditional artistic materials and classical artefacts, the applications of the same techniques to contemporary artworks and related materials (plastics, modern pigments and dyes, etc.) have not been fully investigated. The most widespread alternatives to destructive tests remain very simple methods, such as those based on the evaluation of visual aspect, odour and consistency. This fact explains the particular attention devoted to development, validation and testing of non-invasive methodologies, which could be implemented using portable instrumentation specifically tailored for applications in the conservation field.

Within this framework, optical spectroscopy appears as an ideal candidate to be exploited as working principle in portable tools, tailored for in-situ characterisation of plastics artworks and objects.

Generally speaking, optical spectroscopy includes different techniques that all exploit electromagnetic radiation in the ultraviolet (UV), visible (VIS) and near Infrared (NIR) intervals for investigating the materials. This UV-Vis-NIR radiation can excite electronic and vibrational transitions in the molecular and/or atomic systems constituting the material. These excitation processes may result in selective absorptions of the radiation that impinges the material,





and, hence, the spectral analysis of the out coming radiation provides indications about the molecular groups or atomic species responsible of the observed absorptions. In general, UV-Vis-NIR optical spectroscopy may provide both qualitative (compositional) and quantitative (concentration of selected chemical species) information on the material investigated.

Among the optical techniques available, reflectance spectroscopy demonstrated to be particularly suitable for in-situ non-sampling investigations on several types of materials (Workman and Springsteen 1998), and has therefore become well established in conservation field. Reflectance spectroscopy can nowadays be implemented using different types of portable instrumentations, ranging from handheld devices, to the high-performance portable spectrophotometers equipped with optical fibres up to the most recent imaging instrumentation (Bacci 1995; Mansfield 2002). In particular, the use of optical fibres has led to the development of Fibre Optics Reflectance Spectroscopy (FORS) which is widely recognised as one of the most versatile methodologies for non-invasive analysis in the conservation field. FORS is commonly used for spectral characterisation over the UV-Vis-NIR range.

The analyses of spectra in the UV-Vis-NIR region may be exploited for many purposes. The UV-Vis spectral region is dominated by the absorption bands of the chromophore groups, which are responsible of the colour of the material. In some polymers the insurgence or the disappearance of bands in the UV-Vis spectral interval may be related to degradation of the polymeric chains (e.g. due to photo induced reactions), and the UV-Vis spectrum can provide information about the conservation state of the material. Moreover, the spectrum in the Vis range (380-780 nm) is the basis of colorimetric analysis that is used for quantifying and monitoring the chromatic alterations (discoloration, yellowing, darkening, etc.) due to the ageing processes. Finally, the NIR region (800-2500 nm), characterised by the overtones and combinations bands of the fundamental vibrations of molecular groups, can be useful for discrimination and characterisation purposes.

Practically, different factors (such as the complexity of the materials to be studied, the instrumental performances, the measurement procedures etc.) can condition the actual effectiveness of optical spectroscopy for identification and/or characterisation purposes. One key aspect, for example, is the availability of spectral databases of reference materials, which are necessary for a correct interpretation of data acquired on real objects. Whereas, for many traditional artistic materials (pigments, binding media, varnishes, etc.) several UV-Vis-NIR spectral databases are available, spectral





libraries of polymers of main interest in the conservation field are still lacking. Thus, one of the tasks covered has been the construction of a spectral archive in the UV-Vis-NIR range of the SamCo. This has been considered as the first step in the perspective of a wider use of optical spectroscopy as complementary methodology for identification and characterisation of plastic artworks. Nevertheless, a number of experimental issues and methodological questions related to the specific applications to plastics in the museum context are still open. In the following subsections these aspects are illustrated, by separately considering the study and exploitation of the UV-Vis and the NIR spectral ranges.

UV-Vis spectroscopy

The basics of reflectance spectroscopy can be introduced by considering a radiation beam impinging onto the surface of a non-transparent object. Part of the incident radiation is reflected (diffuse or specular reflections depending on the texture of the surface) at the air object interface, without any change in its spectral distribution. This portion of the reflected signal depends only on the surface properties (roughness) and does not contain any information on the chemical composition. Another part of the incident beam penetrates into the bulk of the sample, where it interacts with the material particles. Selected wavelengths undergo absorptions by the molecular and atomic species and the non-absorbed radiation is scattered and re-emerges from the surface in all the directions (diffuse reflectance). This portion of reflected signal has a different spectral composition with respect to the incident beam and gives information on the material composition. In the visible spectral region, this portion of the reflectance is the coloured light which determines the visual chromatic sensation. The whole reflectance signal includes both the contributions from to the surface and from the volume, respectively. In the reflectance measurements (see details in the technical box on FORS), different geometries of measurement can be used. Normally, when compositional or colour information is sought, only the diffuse reflectance is measured, and the specular reflectance is excluded. Conversely the specular contribution can be of interest for the characterisation of optical properties of the surface, such as the texture, the roughness or the degree of gloss. In applications to the conservation of plastic materials, the measurement of the gloss may be meaningful for the evaluation of the effectiveness of cleaning treatments.

The UV-Vis reflectance measurements on the SamCo were mainly aimed at investigating the practical issues and difficulties related





to the surface characterisation of plastic artefacts. Indeed, the different levels of transparency of many polymers can be a limitation to the use of reflectance spectroscopy. The role of variable gloss and transparency in affecting the reflectance measurements was studied, and practical expedients to deal with the high variability of opacity in plastics objects have been sought. A comparison between different geometrical set up showed that, when possible, the use of high reflecting standard (e.g. Spectralon®) behind the object surface can strongly improve the quality of the spectrum; this is also apparent in semi-transparent plastics. Obviously this methodology can be proposed only for non-bulky objects.

As anticipated above, one of the main uses of the Vis spectrum is the colorimetric analysis. Colorimetry is a complex science aimed at describing the colour perception and related phenomena. It is based on psychological, physiological and physics notions and it is outside of the scope of this work to introduce its basic principles. Nevertheless here it is worth recalling that colorimetric analysis is a widely used tool in conservation field, where it is commonly used for characterising chromatic properties of artistic materials and for quantifying their possible changes with time (Johnston-Feller 2001).

The colorimetric analysis is based on standardised experimental procedures and protocols established by the international organization CIE (Commission internationale d'éclairage) (Wyszecki 2000). The CIE has also defined a theoretical frame (the CIE colour system) to mathematically express the colour of a surface: in terms of numerical coordinates. Suitable colorimetric spaces are defined in which a colour can always be calculated on the basis of tabulated functions once the spectral reflectance in the visible range is known. Actually, different colorimetric systems can be adopted to represent a colour in terms of chromatic coordinates (Marcus 1998). One of the most common schemes adopted, widely used in the conservation community, is the CIE Lab1976 colour system, which is a uniform space specifically conceived to express the chromatic differences as they are visually perceived by humans. In the CIE Lab 1976 system, a colour is represented as a point of coordinates (L^* , a^* , b^*) in a three-dimensional space. The three axes are respectively related to the lightness ($L^* = 100$ is a perfect white and $L^* = 0$ is black), to the red-green ($a^* < 0$ green, $a^* > 0$ red) and to the yellow-blue ($b^* < 0$ blue, $b^* > 0$ yellow) chromatic stimuli. The chromatic difference (ΔE^*) between any two of colours (L_1^*, a_1^*, b_1^*) and (L_2^*, a_2^*, b_2^*), is simply calculated as the Euclidean distance between points them, that is:

$$\Delta E^* = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}$$





This formula may be used to quantify the chromatic distance between two different areas over an object surface (e.g. to map colour non-homogeneities), or also to measure the colour change in time a same point measured.

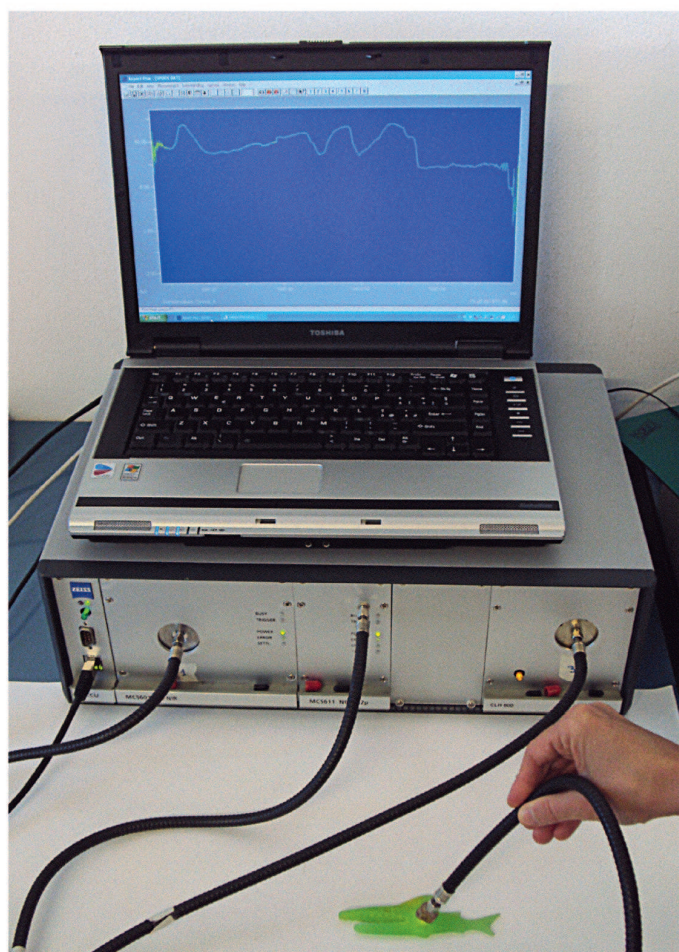
In the study of plastics and polymeric materials, whose optical properties can be finely controlled and varied with an incredible variety of additives, colour cannot be considered an intrinsic property. Hence, in plastic preservation the importance of colorimetry is mainly related to the possibility of monitoring the chromatic alterations in time, as symptoms of degradation phenomena. For example, periodic colorimetric measurements have been performed over a period of about 18 months, to monitor the colour changes of polymers included in mock objects (Polly dolls) exposed in different environmental conditions. The results are discussed in Chapter 2. This experimentation also served to establish an experimental protocol for colorimetric measurements on three dimensional plastic objects.

In principle, colorimetric measurements in objects collections can be performed by means of different type of instrumentation, ranging from colorimeters to portable spectrophotometers. Colorimeters directly provide the colorimetric coordinates and have the advantage of being user friendly and hand held, but they provide poorly resolved spectra and are not suitable for attaining further information. Spectrophotometers, even when portable, are usually less versatile and straightforward, but provide more complete information.

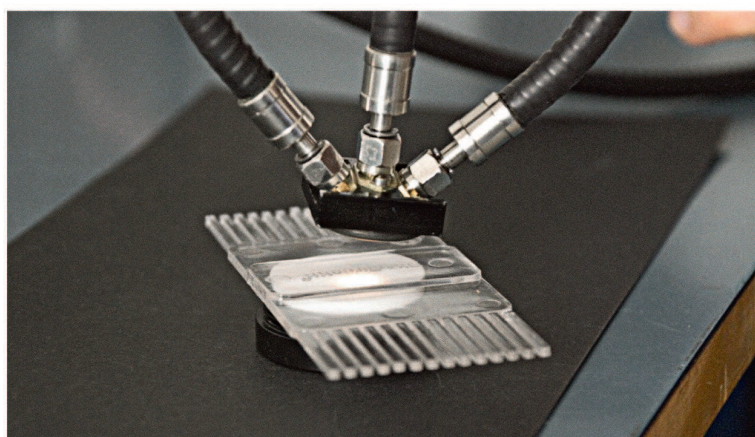
To monitor the chromatic variations in time, it is necessary to ensure the absolute reproducibility of the measurements so as to acquire comparable data on a same point at different times. Colour variations of real objects are expected to be small or moderate under normal exposure conditions, and measurements have to be extremely precise. The exact repositioning of the measurement instrument on the point to be monitored is essential to guarantee reliable data. For these reasons, to control museum objects the recourse to fibre-optics based instrumentation should be preferred to the colorimeters. The possibility of selecting customised probe heads for the specific applications turns out to be crucial to obtaining high quality spectra from measurements on objects (Figures 16).

The acquisition of highly-resolved reflectance spectra in the UV-Vis region is also useful to investigate photo induced phenomena of selected polymers (e.g. expanded polystyrene, EPS) before they become visually appreciable at the naked eye. This was for example the outcome of a study aimed at solving a conservative problem

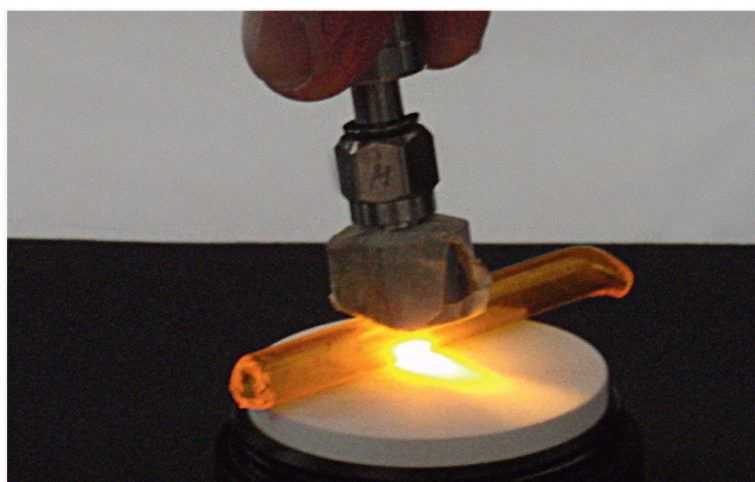




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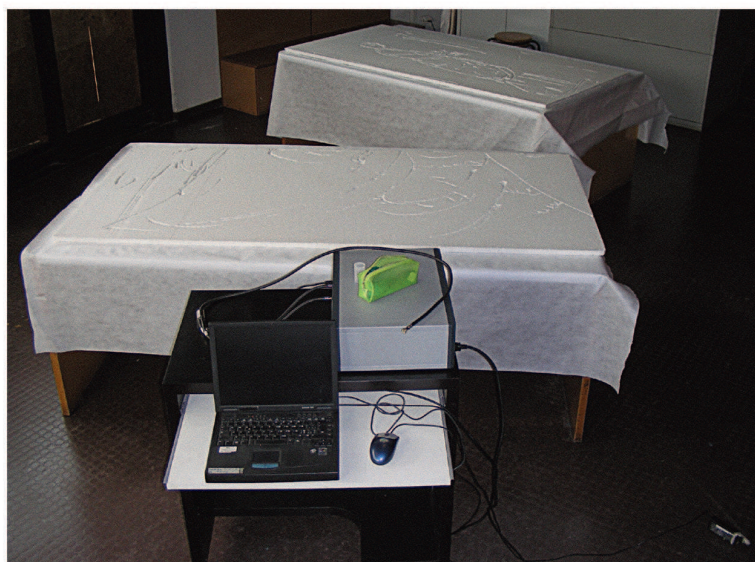
16.b



16.c

Figure 16. a) The portable FORS instrumentation (Spectroanalysers ZEISS mod. MCS601-MCS611) used at IFAC-CNR for the acquisition of UV-Vis-NIR reflectance spectra on SamCo. b) The 2x45°/o° probe-head accessory. c) The 8°/8°probe-head accessory

Figure 17. The portable instrumentation used for the FORS measurements campaign on the EPS artwork “Cartoline” by Stefano Arienti. The artwork, belonging to the permanent collection of the Luigi Pecci Contemporary Art Center (Prato, Italy), was non-invasively investigated in order to map the yellowed areas (photo courtesy IFAC-CNR)



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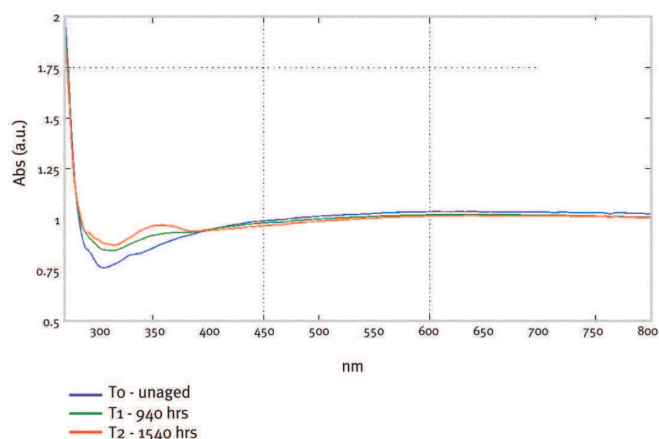


Figure 18. The UV-Vis absorbance spectra of a sample of EPS progressively aged under a halogen light source ($I = 1070$ lux, $U_{\text{v}} 443 = \text{mW/m}^2$). Measurements have been performed on the unaged sample (To), after 940 hours (T1) and after 1540 hours (T2) of exposure

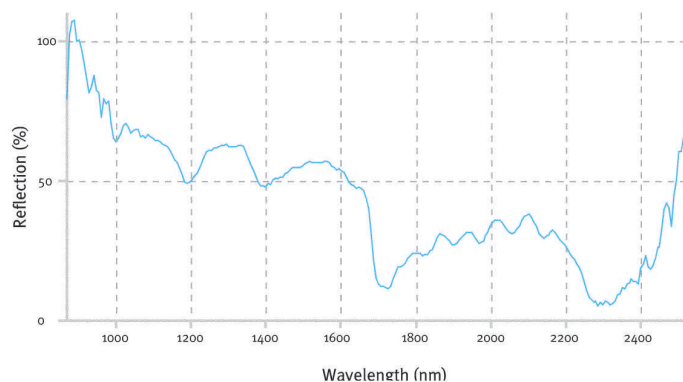


Figure 19. NIR spectrum of cellulose nitrate from the SamCo collection

on an EPS artwork (“Cartoline”, 1990, by Stefano Arienti, from the collection of the Luigi Pecci Contemporary Art Center in Prato, Italy) (Figure 17). Within these investigations a set of artificial light ageing tests were performed on EPS samples using a halogen light source ($I = 1070$ lux). As shown in Figure 18, the UV-Vis spectra measured at different stages of ageing exhibit a progressive alteration in the 300–350 nm interval. These spectral changes were not detectable by means of colorimetric measurements, neither visible with the naked eye. Nevertheless, these alterations appeared to be the early symptoms of the degradation mechanism which causes a progressive yellowing of the material, as confirmed also from a comparison with the measurements performed on the real artwork.

NIR spectroscopy

Near-infrared region of the electromagnetic spectrum (from about 800 nm to 2500 nm) is used in NIR spectroscopy. Absorption of light of these wavelengths induces combination vibrations and overtones of C-H, O-H and N-H chemical moieties in the material. By plotting absorbance versus wavelength absorption spectra are obtained, which are extremely complex in their nature. Unlike in mid-IR region, the bands are typically very broad, consisting of a number of overlapping absorption bands, which makes it difficult to assign specific features to certain chemical components. Instead, mathematical and statistical methods (called also chemometrics) are often utilised to extract information from the information-rich NIR spectra (Figure 19).

The approach typically relies on a development of a large set of calibration samples, which are identified or characterised using analytical techniques. Correlation between the NIR spectral and reference data is then sought using multivariate calibration techniques, such as principal components analysis (PCA), partial least squares (PLS), or artificial neural networks. Obtained correlation is then used to predict the property from a NIR spectrum of an unknown sample.

The quality of correlation will largely depend on the size of the reference sample set, the quality of the reference analytical data, the quality of the recorded spectra and the selected statistical approach.

However, when these limitations are overcome, NIR spectrometry coupled with chemometrics allows for a fast and non-destructive identification of a range of materials and characterisation of their properties.

Despite the advantages, NIR spectroscopy as a single, stand-alone unit only became available in the 1980’s, which is mainly



due to the complexity of the NIR spectra. With the development of powerful personal computers, chemometric software and advances such as fibre-optics, the techniques witnessed a rapid development. It resulted in many commercial applications, ranging from material science, medical uses to astronomy. Portable or online NIR spectrometric techniques have also been developed for identification of modern plastics, and they are extensively used in recycling industry.

The technique was also used for identification and characterisation of various cultural heritage materials, such as paper (Trafela 2007), ink (Strlič 2010), textile (Richardson 2007), even dating of paper have been shown successful (Trafela 2007). However, the only commercial application of the technique has been developed so far for characterisation of historical paper.

A commercial application is needed in order to enable a facile and widespread use of the technique by the conservators and collection keepers in heritage institutions. It can hardly be expected that each institution would analyse an extensive set of historical materials and undergo a highly specialised chemometric approach needed to identify/characterise historic materials.

With this in mind, MORANA RTD d.o.o. is developing a user friendly application, which would enable facile and rapid identification and characterisation of a variety of cultural heritage materials using a single NIR spectrometer. The objective in POPART project was to develop an application for identification of plastics.

In order to build up a reliable identification protocol for plastic materials, a large database of characterised materials is needed, as established above. The use of several different samples of the same plastic increases the reliability of the prediction. Also, the set of various materials should be as broad as possible. It has to be kept in mind that if the unknown material is not in the database used to develop calibrations, erroneous identification is obtained. With this in mind, the SamCo used was expanded with more plastic materials, which were identified using bench top FTIR. NIR spectra were then collected and a statistical model was developed that identified plastics based on the spectral characteristics in NIR region. To further simplify the use of the tool by conservators and curators in museums, demonstration software (MORANA NIR) was developed by Morana RTD d.o.o. based on the statistical method.

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