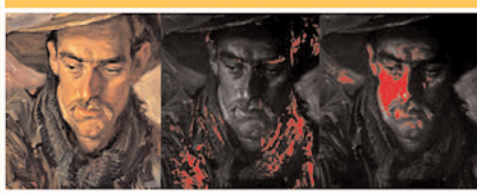
PHYSICAL TECHNIQUES IN THE STUDY OF ART, ARCHAEOLOGY AND CULTURAL HERITAGE

Volume 2



Edited by
DUDLEY CREAGH
& DAVID BRADLEY

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Cover illustration: The images printed on the cover are taken from the chapter by Maria Kubik (Chapter 5) and show a plain photograph and two hyperspectral images of a painting in the collection of the Australian War Memorial.
Left: Photograph of the original painting. *Centre and Right:* Hyperspectral images of the painting, showing the location of pigments of different types used by the artist.

[The image of the painting of an Australian soldier by Ivor Hele was taken with the permission of the Australian War Memorial. The photograph of the original painting was taken by the author in the course of her investigations, and is not an official reproduction of the painting (ART40317) in the Australian War Memorial catalogue.]

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Preface

In this Volume 2 of the series on the use of physical techniques for the study of art, archaeology, and cultural heritage, we continue our policy of choosing topics from widely different fields of cultural heritage conservation. Also, we have chosen authors both in their early and late careers.

In Chapter 1, Dudley Creagh writes on "Synchrotron radiation and its use in art, archaeometry, and cultural heritage studies". He is Professor and a Director of the Cultural Heritage Research Centre at the University of Canberra, Canberra, Australia. He has extensive experience in all aspects of cultural heritage research. *Inter alia*, he was a member of the team responsible for the restoration of the Japanese Zero fighter at the Australian War Memorial, conducted research on prestigious medals such as the Victoria Cross and the Lusitania Medal, investigated the effect of self-organizing alkyl chain molecules for the protection of outdoor bronze sculptures, and studied the properties of lubricating oils necessary for the proper preservation of working vintage motor vehicles. Research groups led by him have studied the mechanisms underlying the degradation of Australian aboriginal bark paintings, and examined of the degradation of iron-gall inks on parchment, dyes and pigments in motion picture film, and dyes and pigments on painted surfaces.

Prof. Creagh has also designed new equipment and devised new techniques of analysis. He designed the Australian National Beamline at the Photon Factory, KEK, Tsukuba, Japan. With Dr. Stephen Wilkins, he also designed the unique X-ray diffractometer (BIGDIFF) mounted on it. He designed a number of its accessories, including an eight-position specimen-spinning stage. For surface studies on *air–liquid* interfaces, he designed an X-ray interferometer for the Research School of Chemistry at the Australian National University. He has designed X-ray interferometers that are now finding application in the phase contrast imaging of small objects. More recently, he has designed the infrared beamline for the Australian Synchrotron, Melbourne, Australia. He is currently President of the International Radiation Physics Society.

In continuation of the theme on synchrotron radiation, Loic Bertrand has elaborated, in Chapter 2, on synchrotron imaging for archaeology and art history, conservation, and palaeontology. Dr. Bertrand is the archaeology and cultural heritage officer at the new French synchrotron, Synchrotron Soleil (Orme les Mesuriers, Gif-sur-Yvette, France). He is charged with the task of raising the awareness of cultural heritage scientists to the use of synchrotron radiation for their research. With Dr. Manolis Pantos, he is responsible for the database that lists all the cultural heritage and archaeological publications involving the use of synchrotron radiation. He is an early-career researcher; but mentioning this undervalues the contribution he has already made to the field, using a variety of experimental techniques. In Chapter 2 he describes a number of his activities as well as the research of others.

In the other chapters of this volume, widely different issues are addressed. Chapter 3 is authored by Ivan Cole and his associates Dr. David Paterson and Deborah Lau. This chapter is concerned with the holistic modelling of gas and aerosol deposition, and the degradation of cultural objects. Dr. Cole is the Deputy Chief of the Novel Materials and Processes Division of the Commonwealth Scientific and Industrial Research Organization (Melbourne, Australia). He has over 20 years experience of being involved in projects concerned with the preservation of cultural heritage. Ivan is an internationally recognized leader in the field of life cycle of materials and the development of protective coatings for metals. In 2004, he was a co-winner of the Guy Bengough Award (UK Institute of Materials, Minerals and Mining). He has taken lead roles in major projects in intelligent vehicle health monitoring for aerospace applications, the relation between building design and climate and component life, as well as the development of performance-based guidance standards and codes for durable buildings. He has made a significant contribution in the application of building and material science to the conservation of cultural buildings and collections. Ivan is a member of international and national committees for research and standards in durable structures.

In Chapter 4, Giovanna Di Pietro describes two different types of experiments she has undertaken in the study of the mechanisms underlying the degradation of photographic media. In the first, she describes the degradation of old black-and-white plates. In the second, she outlines her attempts to understand the mechanisms by which the comparatively modern motion picture film degrades. A significant part of this project involved trying to ascertain exactly which dyes were used by Kodak in their motion picture film from about 1980 onwards. The level of secrecy to which this information was protected was great. And, to this day, no information has officially been divulged by the company, although sufficient information has now been acquired to infer the formulations. Giovanna is a post doctoral researcher at the Institute for the Conservation of Monuments, Research Laboratory on Technology and Conservation Polytechnic University of Zurich, Switzerland. Her current project involves monitoring wall paintings using techniques derived from information technology. Giovanna's other research interests include, *inter alia*, the effect of microclimate on canvas paintings. She is a consultant to museums and archives in the field of photographic preservation.

An entirely new technique for the remote investigation of the pigments in paintings is presented by Maria Kubik in Chapter 5. This technique will significantly enhance the ability of conservators to study the palette of pigments used by artists, check for repairs by others, and detect fraudulent paintings. It complements the techniques described by Prof. Franz Mairinger in an earlier Elsevier book *Radiation in Art and Archaeometry*, edited by Creagh and Bradley (2000). Maria is to receive her PhD from the Australian National University in April 2007. She studied conservation in the Cultural Heritage Conservation Course at the University of Canberra, graduating with the degree of Master of Science, specializing in painting conservation. She is at present the Conservator of Paintings at the Western Australia Gallery.

Dudley Creagh
David Bradley

Chapter 1

Synchrotron Radiation and its Use in Art, Archaeometry, and Cultural Heritage Studies

Dudley Creagh

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Abstract

Synchrotron radiation has become an increasingly important tool for research in the fields of art, archaeometry, and the conservation of objects of cultural heritage significance. Scientists using conventional laboratory techniques are finding that the fundamental characteristics of synchrotron radiation – high brightness, low divergence, and highly linear polarization – can be used to give information not readily available in the laboratory context. In the author's experience, experiments do not translate directly from the laboratory to the synchrotron radiation laboratory: there are subtle differences in the use of what seem to be similar experimental apparatus. To achieve the best results, the research scientist must be able to discuss his or her research aims meaningfully with beamline scientists. And to be able to do this, the research scientist must have an understanding of the properties of synchrotron radiation, and also the various techniques that are available at synchrotrons but are unavailable in the laboratory. The chapter includes a discussion of synchrotron radiation and its properties, monochromators, detectors, and techniques such as infrared (IR) microscopy; soft X-ray spectroscopy; X-ray diffraction; micro-X-ray diffraction and X-ray fluorescence analysis; X-ray absorption spectroscopy (XAS), including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), and X-ray tomography. The underlying principles of these techniques are discussed here. Later in this book, authors will address these techniques in more detail.

Keywords: Synchrotron radiation, IR microscopy, XRD, micro-XRD, micro-XRF, XAS, XAFS, XANES, X-ray tomography.

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Physical Techniques in the Study of Art, Archaeology and Cultural Heritage
Edited by D. Creagh and D. Bradley

1. INTRODUCTION

Synchrotron radiation is an important scientific tool that is becoming increasingly more useful to scientists working in the fields of archaeology, archaeometry, and the scientific conservation of objects of cultural heritage significance. The growth in the number of peer-reviewed research articles by scientists who are using synchrotron radiation is shown in Fig. 1. The data has been taken from a comprehensive compilation of synchrotron articles that is being made by Drs. Manolis Pantos (SSRC, Daresbury) and Loic Bertrand (Synchrotron-Soleil) can be accessed at http://srsdl.ac.uk/arch/publications.html. Both are

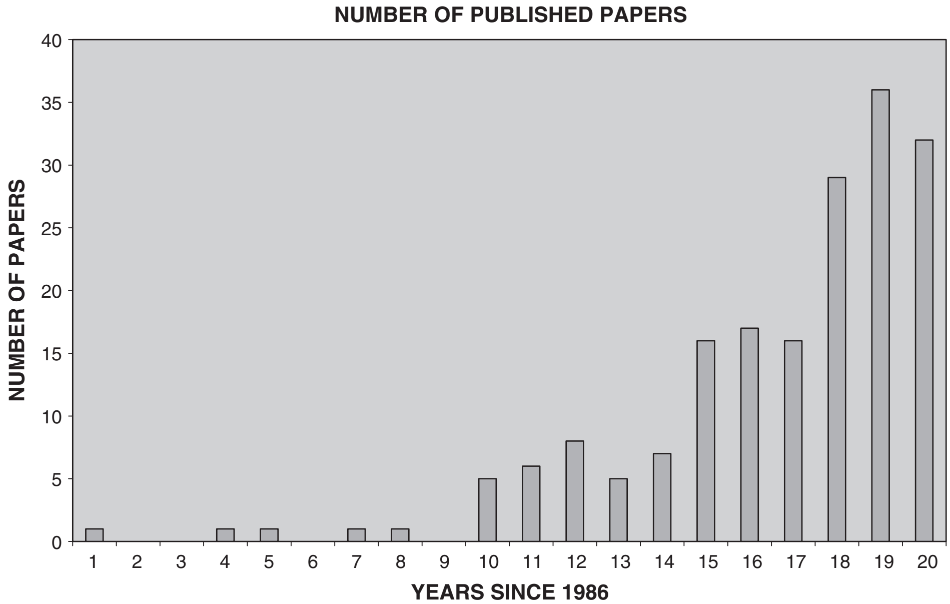

Fig. 1. The growth of peer-reviewed research publications produced by scientists in the fields of archaeology, archaeometry, and cultural heritage conservation since 1986.

contributors to this and later volumes of *Physical Principles in the Study of Art, Archaeology and Cultural Heritage*. The strong growth in publications is mirrored in the increase in the number of workshops held at synchrotron radiation facilities on these topics.

The use of synchrotron by scientists is invariably triggered by the desire to achieve a better understanding of the objects and materials under investigation. And, to a good approximation, the technique chosen is the synchrotron radiation equivalent of a laboratory technique. For example, O'Neill *et al.* (2004) wished to achieve a higher resolution X-ray diffraction pattern from very small amounts of white pigments taken from Australian aboriginal bark paintings than could be achieved using laboratory sources, so that better information could be obtained about the mineral phase composition in the pigments. A laboratory instrument would have required a thousand times more material, and data collection would have taken a hundred times longer. But, as the nature of the problem to be solved became more complex, there arose a need to find other ways to solve the problem – ways that were uniquely suited to the unique properties of synchrotron radiation. The unique properties of synchrotron radiation have enabled the growth of techniques that would not have been feasible in the laboratory situation. A synchrotron radiation source consists of a circulating charged particle beam (usually electrons) in a vacuum vessel (operating vacuum is 10^{-9} mbar) of a high-energy particle accelerator (typically 3 GeV = 3×10^9 eV), and travelling at velocities close to that of light. As will be explained later, radiation is emitted whenever the electron beam is accelerated by the bending magnets that constrain the electron beam to its orbit.

The radiation is highly intense, highly collimated, and highly polarized in the horizontal plane. Also, the emitted radiation covers the whole electromagnetic spectrum: from the far infrared to the hard X region. These unique features have led to the development of many fields of research (XAS, micro-XRD, micro-XRF, and IR microscopy, to name a few) and to the refinement of older laboratory techniques such as XRD and computer-aided tomography. This chapter will include a discussion on synchrotron radiation and its properties.

To devise experiments that will effectively harness the desirable characteristics of synchrotron radiation, it is important to have knowledge of the construction of synchrotron radiation beamlines and of the strengths and limitations of their photon delivery systems. Descriptions will be given of typical beamlines and their monochromators, both of the mirror and single-crystal type, focussing elements, instruments such as diffractometers on which the samples are mounted, and the detectors that collect the scattered radiation. A discussion will be given of such experimental as: infrared microscopy, soft X-ray spectroscopy, X-ray diffraction, micro-X-ray diffraction and X-ray fluorescence analysis, grazing incidence X-ray diffraction (GIXD) and X-ray reflectivity (XRR) techniques, XAS (including XAFS and XANES), and X-ray tomography. The underlying principles of these techniques will be discussed in this chapter. Drs. Bertrand and Pantos will address these techniques in more detail later in this volume, and also in later volumes.

2. THE PRINCIPLES OF SYNCHROTRON RADIATION GENERATION

2.1. Introduction

It is not my intention, in this chapter, to give a full exposition of the principles of synchrotron radiation. That must be reserved for specialized textbooks. See, for example, Atwood (1999), Duke (2000), and Hoffman (2004). Also, Atwood, through the University of California, Berkeley, offers a web-based course on synchrotron radiation (http://www.coe.edu/AST/sxreu).

In this chapter, I shall attempt to present the essence of the subject with little recourse to mathematics. It is assumed that the reader is conversant with the basic notions of electromagnetism. The electromagnetic spectrum arising from the generation of synchrotron radiation ranges from the far infrared (less than 0.1 μm; ~0.1 eV) to hard X-rays (more than 0.1 nm; ~10 keV). The range of interaction is from interactions with atomic and molecular vibrations (far infrared) to crystal diffraction and atomic inner-shell fluorescence effects (X-rays).

The relation between frequency (f), wavelength (λ), and the velocity of light (c) is given by $f\lambda = c$, which can be rewritten as $(h\upsilon)\ \lambda = hc = 1239.842$ eV nm. This expresses the relation in terms of the photon wave packet energy $h\upsilon$. Two useful relations that may assist in understanding some of the figures to follow later are:

- for the energy contained in a photon beam: 1 J = $5.034 \times 10^{15}\ \lambda$ photons (here, λ is the wavelength in nm); and
- for the power in a photon beam: 1 W = $5.034 \times 10^{15}\ \lambda$ photons/s (here, λ is the wavelength in nm).

It is convenient to compare the characteristics of common light sources with those of synchrotron radiation, although at this stage I have not discussed why synchrotron radiation has the properties it has. Table 1 sets out the characteristics of a pearl incandescent bulb, a fluorescent tube used as a replacement for the household incandescent bulb, a typical laboratory laser, and a typical third-generation synchrotron radiation source. It can be seen that the synchrotron radiation source consumes much more source power that the other photon sources.

The photon spectra emitted by both the light bulbs are continuous spectra (although the spectrum of the fluorescent bulb contains the line emission spectrum of the gas used in the bulb). The laser emission is monochromatic, and usually has a small wavelength spread in the emitted line. The synchrotron radiation spectrum is continuous, but, in contrast to the light bulbs that emit in the visible region of the spectrum (less than a decade in wavelength range),

Table 1. Comparison of the characteristics of common light sources (pearl incandescent, bayonet socket fluorescent, common laboratory lasers) with synchrotron radiation sources. The data given is approximate and is given for illustrative purposes only

Characteristic	Incandescent	Fluorescent	Laser	Synchrotron radiation
Source power (W)	100	10	1	10^7
Spectrum	Continuous (0–400 nm)	Continuous (to 400 nm) + discrete spectrum of the fill gas	Monochromatic determined by laser type (1000–400 nm)	Continuous (10 000–0.1 nm)
Source size	Large (2.5×10^3 mm^2)	Large (2.5×10^3 mm^2)	Small (1 mm^2)	Very small (8×10^{-2} mm^2)
Directionality	Omnidirectional	Omnidirectional	Highly directional	Highly directional
Coherence	Incoherent	Incoherent	Coherent	Partially coherent
Polarization	Unpolarized	Unpolarized	Unpolarized	Linearly polarized in horizontal plane mixed polarization off the horizontal plane
Time structure	Continuous	Continuous	Continuous or pulsed	Pulsed

the useful wavelength range of emission is five decades (from far infrared radiation to hard X-ray radiation).

Directionality of emission is an important characteristic of photon sources. Omnidirectional sources emit into all 4π steradians of solid angle. However, in experiments, the experimentalist is usually concerned with illuminating a particular part of their experiment. Let us consider that we wish to illuminate an object 1 mm in diameter, placed 10 m from the source of illumination. Without the addition of optical elements such as focussing mirrors, the fraction of the emission intensity of an omnidirectional source passing through the aperture would be 10^{-8} of the total emission. In contrast, provided the laser was aimed at the aperture, close to 100% of the emitted radiation would pass through the aperture. For a synchrotron radiation source, 100% of the source intensity would pass through the aperture.

Source size is important in two respects. The smaller the source size, the brighter the source is said to be. Also, the size source has an effect on the intensity of the beam at a distance from the source. It is convenient here to introduce definitions related to photon transport that will be used throughout this chapter. They are:

- Flux (F): the number of photons passing a unit area per unit time;
- Brightness (B): photon flux per unit source area per unit solid angle.

Nothing has been said here about the wavelength of photon radiation. For continuous radiation, a slice of the spectrum is taken, usually 0.1% of the bandwidth. When referring to a particular radiation, the definitions of flux and brightness are modified to be:

- Spectral flux (photons/mm^2/s/0.1% BW),
- Spectral brightness (photons/mm^2/mrad^2/s/0.1% BW),
- Spectral flux per unit solid angle (photons/mrad^2/s/0.1% BW), and
- Spectral flux per unit horizontal angle (photons/mm^2/mrad/s/0.1% BW).

Note that, according to Liouville's theorem, flux and brightness are invariant with respect to the propagation of photons through free space and linear optical elements. They are the best descriptors of source strength.

Coherence is related to the ability of radiation emitted from different parts of the source to have fixed passes in relation with one another. Longitudinal coherence length is defined as

$$L_{\mathrm{coh}} = \frac{\lambda^2}{2\Delta\lambda}$$

Thus, an optical laser has high coherence since λ is typically 633 nm and $\Delta\lambda$ is less than 0.1 nm ($L_{\mathrm{coh}} = 2 \times 10^6$ nm), whereas a light bulb would have typically 600 nm and $\Delta\lambda$ is perhaps 800 nm ($L_{\mathrm{coh}} = 225$ nm). The question of coherence in the case of synchrotron radiation is not quite so straightforward: it depends on the method of production of the synchrotron radiation.

Of the radiation sources, only synchrotron radiation sources produce polarized radiation. Synchrotron radiation is normally 100% linearly polarized in the plane of the electron orbit, but, as the view of the radiation changes, so does the degree of linear polarization.