ual: university of the arts london

Title	Teaching and Professional Fellowship Report 2002/3 : Fourier Transform Infra Red (FTIR) Spectroscopy
Type	Report
URL	http://ualresearchonline.arts.ac.uk/492/
Date	2003
Citation	Yianni, Mike (2003) Teaching and Professional Fellowship Report 2002/3 : Fourier Transform Infra Red (FTIR) Spectroscopy. Project Report. University of the Arts London, London.
Creators	Yianni, Mike

Usage Guidelines

Please refer to usage guidelines at http://ualresearchonline.arts.ac.uk/policies.html or alternatively contact ualresearchonline@arts.ac.uk.

License: Creative Commons Attribution Non-commercial No Derivatives

Unless otherwise stated, copyright owned by the author

Fellowship Report July 2003

FTIR Spectroscopy

Michael Andrew Yianni MSc

Index

Page

Introduction

The fellowship provided the opportunity to develop skills in Fourier Transform Infra red Analysis. The Nicolet Avatar 360 FTIR spectrophotometer, supported by Nicolet Omnic 5a software, provided the measuring and processing tools.[1] These were used to produce absorption spectra of a wide range of materials used by artists. Spectra produce also contributed to studies of the effects of various conservation treatments on the chemical structure of cellulose, the main component of paper from natural sources.
Students ranging from BA, Pg.Dip, MA and Ph.D. found the application of the technique useful to their studies.

Fellowship Goals

The goals of the fellowship were:

- To apply for and to satisfy the membership requirements of the conservation scientists international infrared users group (IRUG)
- To set up a live data bank of FTIR spectra of artist materials
- To develop skills and expertise in the technique
- To provide support to both teaching and research

Position reached on Goals

Membership of IRUG

Spectra required for membership of the IRUG have been produce and forwarded to the Chairperson, Boris Pretzel of the Victoria and Albert museum. A total of twelve spectra converted to the required electronic format were submitted on 19 June 03.[2] Examples of the spectra submitted are included in this report. Membership of the group should be agreed in the near future.

FTIR Spectra Data Bank

Why a Data Bank?

In order to answer the question a simple brief explanation of Infrared (IR) spectroscopy is required. When infrared radiation is passed through a sample some of the radiation may be absorbed and some of it passed through (transmitted). A Fourier transform infrared spectrometer detects and measures the absorption of the radiation simultaneously over the entire frequency range of the radiation. A computer attached to the spectrophotometer interprets the intensity of absorption by the sample as a peak at the frequency of absorption. The intensity of absorption determines the size of the peak. The computer will produce a spectrum, a pictorial representation of absorption peaks, over the frequency range. Interatiomic bonds within the sample give rise to the absorption of the IR radiation. Bonds in different molecular environments absorb at varying intensities and at varying frequencies. The absorption gives rise to bond bending and stretching vibrations. The stretching vibration requires the absorption of more radiation then bending and will produce a stronger peak. The type of functional group, interatomic bond, the molecular structure/environment will determine the frequency of absorption. Characteristic absorptions, intensities will occur within a narrow range i.e.

Alkyl C-H stretching 2950-2850 cm^{-1} (strong absorption)

Alcohol/Phenol O-H 3550-3200 cm^{-1} (broad peak, strong absorption).[3]

However the characteristic absorption intensity may vary depending on the bond, molecular environment. Also strong absorption can mask weak absorption within a mixture.[4] Taken together with the sometimes unique combinations of materials used in artifacts. The chemical and physical changes that can occur to such materials over time. Makes identification of these materials from first principles (assigning absorption peaks to functional groups, bonds etc.)

extremely difficult. Therefore production of known spectra for comparison becomes the preferred option for identification.

The data bank has been set up and the web site constructed to support and to disseminate spectral information. It is hoped to go live very soon. The data bank, which stands at over 150 spectra will be developed and added to over the next few years. The majority of the spectra are of individual compounds. This is a necessary first stage. The initial choice of materials to be analysed was based on materials currently held, used, in the Conservation section of the Camberwell College of Arts. The materials analysed are from a period that spans 20 years. Expanding the quantity of spectra, of the combination of artist materials, in the data bank is the next stage. Artificial ageing, as described later in this report, will also be carried out on the materials and the spectra collected and added to the data bank. Examples of spectra produced are included at the back of this report.

All spectra were obtained using 200 scans at a resolution of 4cm-1 with DTGS KBr detector using Happ-General Apodization.

The construction of the web site also helped to develop my skills in the use of image and web design software, which were very limited. This was on the whole achieved by engaging with the software. The web site should go live within the next two weeks. The site will be located at www.Research.linst.ac.uk/cons managed by Dr. Angie Geary.

Development of skills and expertise

Analysis by FTIR is not with out problems. Preparation of the sample for analysis is crucial to obtaining good quality spectra.
The FTIR spectra were obtained by the production of KBr (potassium bromide) pellets containing approximately 0.5 % by weight of sample. KBr is transparent to IR and will not absorb in the mid infrared region

400 to 4000 cm-[1]. The material to be analysed, 1mg, was ground with 250 mg of KBr and pressed into a disc using an evacuated die and a hydraulic press at a pressure of 10 tons.[5] The disc produced was then inserted into the analysing sample compartment of the spectrophotometer and the spectra obtained.

Water absorption by the sample or the KBr can interfere with the production of well-resolved spectra. The water will give a large broad absorption peek and can obscure other characteristic peeks. Ensuring that the KBr, the sample and the disc did not contain water absorbed from the environment proved to be very difficult. Grinding of the sample with KBr, using an agate mortar and pestle, is to ensure even dispersion and very small particle size with out contamination. The presence of water will greatly reduce the efficiency of grinding leading to unresolved spectra. All the above problems were encountered even though steps were taken to reduce the possibility of water absorption. Desiccators containing silica gel drying agent were used to store the die, KBr, weighing vessels in order to minimise the problem. Samples were also pre dried under vacuum of 1000 mbar at a temperature of 70° C prior to grinding. The die was also evacuated during the 10-minute period required for pressing the disc.
By using an evacuated vacuum oven a lower sample drying temperature was required. This reduced the risk of degradation of the sample while minimising the problem of water.

Attempts were made to develop simple alternative methods to KBr that could be employed without the need to purchase expensive attachments. Most failed to produce well-resolved spectra. Casting of films into a disposable KBr disc holder was also tried. Initially the film produced contained air pockets and was of a non-uniformed thickness. However by using a microscope slide covered with silicon release paper it was possible to obtain a film that overcame the above problems and produced a well resolved spectra.

The disposable KBr disc holder contains a circular indentation the same size radius as the disc. The disc is held in position over the IR pathway slit by a pressure sensitive adhesive. The indentation was used as a mould for casting of the films.

Another method attempted was to cast films on to melinex film (polyethene terapthalate) and to measure the combined absorption. The melinex IR absorption spectrum was first measured without any sample. The computer software was then used to subtract the melinex absorption spectra from the combined spectra. The remaining absorption peeks can then be attributed to the film. However this did not prove to be successful and more work will have to be done to refine this method of offering up the sample.

Alternative FTIR sampling techniques

There are a number of alternative techniques that would enhance the collection of spectra by improving the interface and interaction between the infrared beam and the sample. The potassium bromide pellet technique has its limitations. The sample has to be composed of material that can be ground with the KBr to give a homogeneous pellet of very small particle size. Adhesives, gels, gums, pastes, soft powders, soft polymers, rubbers for example do not normally lend themselves to grinding. There are devices available based on the following techniques that overcome the limitations of the KBr pellet technique. Attenuated total reflection (ATR), diffuse reflectance (DR), and specular reflectance/reflection-absorption techniques (SR-RA). Each technique has its limitations but taken together the range of materials that can be analysed increases significantly. ATR, DR, SR-RA techniques will allow for analysis of gels, pastes, soft polymers, soft powders, surface coatings, full range of liquids and biological samples.[6]

The section is in possession of a video imaging FTIR microscope the Nicolet Inspect IR Plus. It combines attenuated total reflectance, external reflection and transmission microanalysis

capabilities with video microscopy. The one draw back is the requirement to cool the detector with liquid Nitrogen.

The use of the microscope has been limited for this reason. It is planed to develop its use over the next year offering even more possibilities for analysis.

To provide support to both teaching and research

The technique has been used to support Undergraduate and Postgraduate Conservation research projects. The technique was used in the following projects:

- Identification of Madder as the colouring material in a pair of hats. BA final year project for the conservation of two Tudor flat hats.[7]
- To identify the varnish used on a jewellery box. The varnish was shown to be Shellac based. MA research project.[8]
- To measure the possible change to the crystallinity index within the amorphous regions of cellulose as part of the study of the effects of washing on paper. MA research project.[9]
- To study the effects of dye fixing agents on cellulose. MA research project.[10]
- Analysis of dust samples for Ph.D. research thesis.[11]

The Crystallinity Index of Cellulose.

The measure of the Crystallinity Index (CI) of cellulose will be employed in the near future to assist a doctoral research student look at the effect of various Conservation treatments on Jap tissue.

The CI is the ratio of the intensity of the IR absorbance bands at 1372 and 2900 cm^{-1} of the cellulose molecular vibrations. The two bands in question, 1372cm^{-1} due to C – C deformation and 2900cm^{-1} due to C - H stretching will change in intensity with any change in the crystalline arrangement of the cellulose units. A decrease in the amorphous regions and

subsequent increase in crystallinity has been postulated as an indication of embrittlement. This results in the loss of tensile strength, toughness, for paper made from cellulose.[12]
The CI was measured for four paper samples. The paper used was made from 100% rag (cotton). Two of the samples were subjected to five one hour cold tap water immersion washes. The washed samples were air dried at
23°C at 55% relative humidity (RH). A washed sample and an unwashed sample were then artificially aged by placing in an environmental oven set at 80°C, 65%RH for 1 month. The other two samples, one washed the other unwashed were stored in an environmental chamber set at 23 °C 55% RH for the period of ageing of the other samples. At the end of the month there were two groups of samples. Group 1 containing: unwashed unaged sample and a washed unaged sample. Group 2 containing unwashed aged sample and a washed aged sample.

Measurement of intensities of absorption for the calculation of the CI.

The four group samples were then dried under vacuum at a temperature of
70°C for 8 hours. At the end of the 8 hours the samples were placed in a desiccator cabinet for 20 minutes to cool to room temperature. Twelve KBr disc were then prepared, three discs for each of the group samples and the absorption spectra measured. The base line of the cellulose spectra was then corrected. The base line of the band at 1372 cm^{-1} was set to zero at 1400 and 1350cm^{-1}. The base line of the band at 2900cm^{-1} was also set to zero at 3000 and 2750 cm^{-1}. The absorption intensities were determined and the CI was then calculated for the 12 samples. The mean values of the CI results for each of the four group samples were then calculated. The results were then subjected to an analysis of variance (ANOVA) using sigma stat 2.03 software.

The following results were obtained:

Group	Crystalline Index Value

Unwashed and Unaged	0.944
Unwashed and Aged	0.939
Washed and Unaged	0.936
Washed and Aged	0.920

Taking into account all possible errors no significant difference in CI was detected between the groups of samples. This was probably due to the stability of the cotton cellulose, which is known to be high in alpha cellulose content. Cellulose chains can be composed of alpha cellulose, beta cellulose and gamma cellulose. Gamma cellulose is degraded short chain cellulose that is soluble in water. Beta cellulose chains are insoluble in water but soluble in dilute acids and alkalis. Alpha cellulose chains are only soluble in concentrated alkali. The above confirms why the paper of books, the paper of drawings, manuscripts and prints made from cotton have stood the test of time. That is they have undergone very little degradation over hundreds of years.

Conclusion : Fellowship Experience

The fellowship has been a very positive experience. I have developed my Analytical, IT and Personal skills. Without the fellowship it would not have been possible to carry out the work and lay the base for future work. The work completed has set up the conditions to achieve all the fellowship goals before the start of the next academic year.

There were initially a number of problems but they were on the whole resolved. This also proved to be a positive learning experience.
However I would advise anyone against even contemplating trying to fit the fellowship into parts of the working week as an alternative to taking a sabbatical!

To conclude I would like to thank the Institute, the panel, staff and students at Camberwell, especially within Conservation. I feel very honoured to have had this wonderful opportunity.

1 Nicolet Instrument Ltd.
Budbrooke Rd
Warwick CV34 5XH
England.

2 JCAMP-DX Spectral File Format for Submissions to the Infrared &Raman Users Group (IRUG) Database. IRUG 2002. www.irug.org
3 , 4 Skoog, West and Holler. Fundamentals of analytical Chemistry. 5th edition. 1988. ISBN 0-03-14826-6
5 R.R.Hill and D.A.E.Rendell The Interpretation of Infrared Spectra. 1975 Heyden & Son Ltd. ISBN 0 85501 066 5
6 Infrared Spectroscopy. JAIC Volume 30 article No. 1. Londa J Larson. 1991
7 BA Conservation Project. 2003 Julie Botticello BA
8 MA Dissertation 2003.
9 MA Dissertation 2003.
10 MA Dissertation 2003. Ronald Pace MA
11 Current Ph.D. research. Zoe Gail Tillotson.
12 Atalla. The crystallinity of cellulosic fibers. 1981. Advances in Chemistry ACS.