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Journal of the Canadian Association for Conservation (J. CAC), Volume 30

J.CAC is a peer reviewed journal published annually by the Canadian Association for Conservation of Cultural Property (CAC), PO Box 87028, 332 Bank Street, Ottawa, Ontario K2P 1X0, Canada; Tel.: (613) 231-3977; Fax: (613) 231-4406; E-mail: coordinator@cac-accr.com; Web site: http://www.cac-accr.ca.

Journal de l'Association canadienne pour la conservation et la restauration (J. ACCR), Volume 30

Le *J.ACCR* est un journal révisé par des pairs qui est publié annuellement par l'Association canadienne pour la conservation et la restauration des biens culturels (ACCR), BP 87028, 332, rue Bank, Ottawa (Ontario) K2P 1X0, Canada; Téléphone : (613) 231-3977; Télécopieur : (613) 231-4406; Adresse électronique : coordinator@cac-accr.com; Site Web : http://www.cac-accr.ca.

Web-based Infrared Spectral Databases Relevant to Conservation

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Infrared spectroscopy is one of the most useful analytical methods available to art conservators today. This cost-effective method can be used to identify most organic as well as some inorganic compounds (most binders, fillers, and also some pigments); however, it is impossible to do this without reference spectra. Besides the commercial infrared (IR) spectral databases, there are numerous free infrared spectroscopy resources on the World Wide Web. This paper discusses several of such very good, and freely accessible, IR spectroscopy resources that cover most of the needs of conservators; some of the best-known commercial IR spectral databases are also reviewed. The focus of this paper is mostly on the spectra of traditional materials (mostly pre-20th century artists' materials). The paper also discusses a number of recent articles that are related to material studies and present various useful spectra for conservation purposes. Many of the sites discussed will be known to experienced infrared spectroscopists, but it is hoped that this paper will be a useful review of reference resources for museum professionals new to the field of infrared spectroscopy.

De nos jours, la spectroscopie infrarouge est parmi les méthodes analytiques les plus utiles dans le domaine de la restauration d'oeuvres d'art. Relativement peu dispendieuse, cette technique permet d'identifier la plupart des composés organiques ainsi que certains composés inorganiques (par exemple, la plupart des liants, des charges et aussi certains pigments). Cependant, l'identification de ces matériaux est impossible sans accès à des spectres de référence. Cet article passe en revue plusieurs excellentes ressources spectroscopiques gratuites disponibles au grand public sur la toile électronique mondiale (world wide web), lesquelles devraient pouvoir répondre à la plupart des besoins des restaurateurs. L'accent est mis sur les sources pouvant fournir des spectres de matériaux d'artistes traditionnels (antérieurs au XXe siècle). D'autres sources, telles les bases de données commerciales de spectres infrarouges les plus connues, sont aussi passées en revue. Quelques articles récents portant sur l'étude des matériaux et présentant des spectres infrarouges utiles en restauration sont aussi abordés. Les spécialistes en spectroscopie infrarouge seront déjà familiers avec la majorité des ressources discutées dans cet article; le but est plutôt de fournir aux professionnels des musées qui sont moins aguerris dans le domaine de la spectroscopie infrarouge, une vue d'ensemble utile des sources de référence qui leur sont disponibles et abordables.

Manuscript received March 2005; revised manuscript received November 2005

Introduction

Analysis of artifacts before conservation is becoming increasingly common. A knowledge of the composition of the original materials is very helpful for choosing suitable materials for conservation work. Infrared (IR) spectroscopy is one of the well-established methods of analysis in conservation science[1]. Many conservation centers have IR spectrometers and people who are trained to run them. Because the vast majority of artists' materials (for example: pigments, fillers, oils, waxes, resins and proteins) absorb infrared radiation, they can be analyzed with IR spectroscopy. The popularity of IR spectroscopy is further enhanced by the small sample size required (a few mg to several tens of mg depending on the material), the almost non-destructive nature of the analysis, cost-effectiveness (because of the relatively low cost of the equipment, low maintenance and running costs) and short time needed for the analysis.

Infrared spectroscopy, as an analytical tool, has undergone extensive instrumental and methodological developments over the past two decades. The advances in IR microspectroscopy[1,2] and IR imaging allow for the study of extremely small samples, a consideration when studying cultural objects, and the mapping of spectral features over surfaces, which permits the gathering of highly localized information about sample composition. The reflectance[3] techniques[1, 4] allow for the study of difficult samples (i.e. those not suitable for transmittance[5] measurements). In spite of these developments, the actual interpretation of infrared spectra is still conducted by comparing them with reference spectra. This is because the theoretical description of infrared spectra is still far from the level needed for accurate prediction of IR spectra of complex materials. Thus, the availability of reference spectra is very important and infrared spectral databases are an integral key to the use of this analytical technique.

The high price of commercial IR spectral databases means that for smaller research groups and labs where use is only occasional, the purchase of a serious commercial IR spectral database is usually beyond budget limits. In such cases of limited or occasional use, it is very reasonable for conservators or conservation scientists to exploit the free and readily accessible resources on the World Wide Web.[6] The most important and conservation-relevant infrared spectral collections are reviewed here, as are some of the leading commercial IR databases. In addition to the commercially available and free web-based IR spectra, a number of very useful publications, including articles and dissertations related to material science, discuss IR spectral information useful to conservators. Many if not all of these publications are available both in print and electronically.

This paper focuses mostly on the IR spectra of the traditional pre-20th-century artists' materials (pigments, binders, fillers, etc.). The usefulness for art conservators of a selection of web-based IR spectral resources was assessed by searching the spectra for a group of materials relevant to the selected area of conservation. The test-set of materials includes: oils (linseed oil and sunflower oil), waxes (beeswax and carnauba wax), natural resins (dammar resin and shellac), proteinous materials (casein and fish glue or isinglass), carbohydrates (gum arabic and starch) and pigments (yellow ochre, smalt, ultramarine, red ochre or iron oxide red, malachite, green earth, umber, chalk, and basic white lead carbonate).

It is important to keep in mind that even if reference spectra are available, interpretation of infrared spectra requires experience and judgment. Computerized search-match programs do not generally work well for complex mixtures and for aged or degraded materials. In addition to consulting reference spectra, acquiring infrared spectra of reference materials with the same instrument and parameters as an unknown sample can be very helpful.

Commercial IR Spectral Databases

Table I presents information on the availability of the IR spectra of the test-set of materials in the commercial databases described below.

Bio-Rad Sadtler's HaveItAll IR

Bio-Rad Sadtler's HaveItAll IR[7] is an excellent and perhaps the best known IR spectral database. It gives access to over 220,000 IR spectra covering a very broad selection of compounds and materials (including pure organics, inorganics, organometallics, polymers, and various industrial compounds). All the spectra can be accessed from a CD or via a secure web connection. The database contains numerous spectra with conservation relevance.

Bio-Rad Sadtler offers various pricing schemes for this database. One of them is a limited-time access (one year) that offers text and structure searching capacities.[8] This licence allows the user to perform exact material identifications and to classify and characterize unknown materials. Those users who search only occasionally can exploit another costed option: the pre-paid Hit List Keys pricing system. This allows an unlimited number of searches within the entire database. However, by default, the user can see only the matching spectra, but not the identity of the compounds. In order to reveal this, it is necessary to use the pre-paid keys, one per compound.

Bio-Rad Sadtler also makes numerous sub-collections of spectra available through individual sales. Several of these, for example "Dyes, Pigment and Stains", "Fats, Waxes and Derivatives", "Minerals and Clays" and "Adhesives and Sealants" have direct and obvious relevance for conservation.

FTIRsearch.com

Another very powerful commercial online IR spectral database is the FTIRsearch.com.[9] FTIRsearch.com is co-sponsored by Thermo Electron's Informatics and Services Group and Molecular Spectroscopy Group to provide access to spectral databases. With FTIRsearch.com, it is possible to access over 71,000 FTIR and almost 16,000 Raman[10] spectra in the Thermo Electron and Sigma/Aldrich spectral databases. The collection consists of numerous industry-specific sub-collections (for example polymers and pharmaceuticals). Some of the sub-collections contain spectra with relevance to conservation, for example pigments and binders. Most of the spectra of pigments in this database are for organic pigments. The spectra for inorganic pigments are few to none, so that most of the pigment spectra in this database are not directly relevant to the identification of pre-20th-century artists' materials. The binder materials in this database also tend to be modern; spectra of aged materials are absent.

The pricing structure at FTIRsearch.com is credit-based with price depending on the number of credits purchased.[11] Every text (name or keyword) search costs 10 credits and each spectral search amounts to 25 credits.

FDM Electronic Handbook of FTIR Spectra

The commercial database FDM Electronic Handbook of FTIR Spectra[12] provides over 6,000 condensed phase and over 5,000 vapour phase FTIR spectra. The database consists of IR spectra of organic compounds (950 spectra), polymers (580 spectra), surfactants (430 spectra), drugs (3750 spectra), and mineral and inorganics (310 spectra). These sub-collections can be bought separately (for example the 310 spectra of mineral and inorganics), or as a complete IR spectra collection (11,240 spectra). The number of conservation-related materials in this database is small.

S. T. Japan Spectral Library

A good commercial IR spectral library is the S. T. Japan Spectral Library,[14] which contains several sub-databases: the ATR/FTIR Aldrich-Ichem Package Database containing about 25,470 spectra; the SDBS FTIR Database containing 50,000 spectra; and the Raman Database containing 4,000 spectra. As is the case for other databases, thematic subsets may be bought separately; for example: the Dyes, Pigments and Stains Library with 845 Spectra and the Polymer and Polymer Additives Library with 1,124 spectra.[15] The database is oriented primarily towards organic and industrial chemistry, and numerous spectra of binder materials are available. The database contains only a few spectra of minerals and inorganic pigments that are used in conservation, however.

Freely Available Infrared Spectral Databases on the Web

Free, online IR spectral databases are reviewed in this section. **Table II** presents information on the availability of the IR spectra of the test-set of materials.

IRUG – the Infrared and Raman Users Group

The Infrared and Raman Users Group (IRUG)[16] is an initiative of conservation professionals to create a forum whereby infrared and Raman spectra can be freely exchanged for the study of cultural heritage. IRUG focuses on the development of this collaborative database of spectra of artists' and related materials. The database contains about 1,250 spectra of various oils, waxes, natural and synthetic resins, dye materials, proteins, gums, pigments and minerals. Individuals and institutions from the conservation field donated their spectra to the database. The

Table I. Availability of the IR Spectra of Materials Relevant to Conservation in Commercial IR Spectral Databases.
The availability of the spectra is given as follows: +++: more than 3 spectra; ++: two to three spectra; +: one spectrum; - no spectra.

Groups of Binders and Pigments	Compounds	Bio-Rad Sadtler's HaveItAll IR	FTIRsearch	FDM Electronic Handbook of FTIR Spectra	S. T. Japan Spectral Library
Oils	Linseed oil	+++[a]	++	+	+
	Sunflower oil	+	+	-	+
Waxes	Beeswax	+++	-	-	+
	Carnauba wax	+++	++	+	+
Natural resins	Dammar resin	-	+	-	+
	Shellac	-	++	-	+
Proteins	Fish glue (or isinglass)	-	-	-	-
	Casein	+	+	-	+++
Carbohydrates	Gum arabic	-	+	-	+
	Starch	+	+++	-	++
White pigments	Chalk [$CaCO_3$]	++	-	+	++
	White lead [$2PbCO_3 \bullet Pb(OH)_2$]	+	-	-	-
Yellow pigment	Yellow ochre [$Fe_2O_3 \bullet H_2O$]	++	-	-	-
Red pigment	Iron oxide red (red ochre) [Fe_2O_3]	+++[b]	-	-	+
Blue pigments	Smalt [$K_2O \bullet SiO_2 \bullet CoO$]	-	-	-	-
	Ultramarine [$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$]	+++[b]	-	-	+
Green pigments	Green earth (celadonite and glauconite) [Fe, Mg, Al, K, hydrosilicate]	-	-	-	-
	Malachite [$CuCO_3 \bullet Cu(OH)_2$]	+++[b]	+++	-	++[b]
Brown pigment	Umber, burnt [Fe_2O_3+MnO_2, clay, etc.]	-	-	-	-

[a] Several spectra of different grades of linseed oil (cold pressed, refined, etc.).
[b] Several spectra, some of them with additives.

spectra are evaluated by professionals knowledgeable in IR spectroscopy, to ensure their quality, before inclusion in the database.

The spectra in the IRUG Spectral Database (Edition 2000) are presented in the customized IRUG-JCAMP-DX format developed to ensure file uniformity and the inclusion of both numerical data and descriptive text into the spectral files. The spectra can also be viewed and printed out. IRUG files contain important details such as sample age, colour, source, formula, detector limits and sample preparation. The spectra are presented using the absorbance[4] scale rather than transmittance. In most cases the wavenumber[17] range for the spectra of binders (for example oils and waxes) is 4,000 to 400 cm^{-1}. The wavenumber range for spectra of pigments and minerals is primarily 4,000 to 600 cm^{-1}, but in a few cases, also 4,000 cm^{-1} to 500 cm^{-1}. IRUG Edition 2000 is keyword-searchable using a material's full or partial name. Search results are presented in tabular form giving the number of the spectrum, the name of the material or the mixture and the name of the contributing institution.

Clicking on the spectrum number opens the absorbance spectrum. Above the main spectrum there is a small spectrum that presents the expanded wavenumber range 1,850-650 cm^{-1}.

Since this database was created by conservation scientists themselves, it is focused on materials relevant to conservation. A very useful feature of this database – absent in most others – is the availability of the IR spectra of aged materials. These are mostly carbohydrates (i.e. tragacanth gum and karaya gum), natural resins (i.e. dammar, amber varnish and yellow shellac), organic dyes (i.e. saffron) and proteins (i.e. gelatine and egg yolk). In many cases, materials of different geographic origin are presented; for example, there are 21 different IR spectra of dammar from various locales and ages. When dealing with artifacts, this can be critical, as real-life materials are almost never completely pure and often they do not have a very well-defined composition. The availability of different spectra (having slight differences in composition and impurities) can be of great help in spectral interpretation.

Another advantage of this database is the availability of the 324 spectra of mineral pigments, which are not as common in IR spectral databases as the spectra of organic compounds.

In our opinion the IRUG database is the single most useful IR spectral database for conservation-related applications.

SDBS

SDBS[18] is a spectral database system for organic compounds that was set up and is maintained by the National Institute of Advanced Industrial Science and Technology (NIAIST) in Tsukuba, Ibaraki, Japan.

Table II. Availability of the IR Spectra of Materials Relevant to Conservation in Free IR Spectral Databases.
The availability of the spectra is given as follows: +++: more than 3 spectra; ++: two or three spectra; +: one spectrum; -: no spectra.

Groups of Binders and Pigments	Compounds	IRUG	SDBS	FT-IR Spectra at UT	The NIST Webbook	IR Spectra at Sigma-Aldrich
Oils	Linseed oil	+++[a]	-	+++[b]	-	-
	Sunflower oil	+	-	+	-	-
Waxes	Beeswax	+++[a]	-	+	-	+++[a]
	Carnauba wax	+++[a]	-	-	-	+
Natural resins	Dammar resin	+++[a]	-	+	-	-
	Shellac	+++[a]	-	+	-	-
Proteins	Fish glue (or isinglass)	-	-	+	-	-
	Casein	+	-	-	-	-
Carbohydrates	Gum arabic	+++	-	+	-	-
	Starch	++	-	+	-	-
White pigments	Chalk [$CaCO_3$]	++	+	+	+	-
	White lead [$2PbCO_3 \bullet Pb(OH)_2$]	+++	-	+	-	-
Yellow pigment	Yellow ochre [$Fe_2O_3 \bullet H_2O$]	++	-	++[c]	-	-
Red pigments	Iron oxide red (red ochre) [Fe_2O_3]	+++[d]	-	++[d]	+	-
Blue pigments	Smalt [$K_2O \bullet SiO_2 \bullet CoO$]	++	-	+	-	-
	Ultramarine [$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$]	+++[a]	-	++	-	-
Green pigments	Green earth (celadonite and glauconite) [Fe, Mg, Al, K, hydrosilicate]	+++	-	+	-	-
	Malachite [$CuCO_3 \bullet Cu(OH)_2$]	+++	-	+	-	-
Brown pigment	Umber, burnt [Fe_2O_3+MnO_2, clay, etc.]	-	-	++[c]	-	-

[a] Several spectra of different grades of the material (for example, linseed oil: cold pressed, refined, etc.; beeswax: crude, bleached, etc.).
[b] Spectra of aged samples of linseed oil.
[c] Several spectra, some of them with additives.
[d] Several different types of ochre, of which several are red ochres, although not labelled as such.

This is a very large and powerful database providing not only IR spectra but also spectra of various other spectroscopic techniques. There are currently 49,800 IR spectra listed, most of which have been measured at the NIAIST laboratories. The majority of the compounds in this database are obtained from commercial companies and sources. SDBS is a spectral database system primarily for common organic compounds, but it also includes spectra of a few inorganic compounds of use to conservation professionals (see **Table II**). Only a few binders are given (oils, resins, etc.). Liquid samples have been measured using the liquid film method and solid samples have been measured using the KBr disc or Nujol mull methods.

The SDBS database allows for the search of compounds and also spectral searches. It is possible to search by compound name, molecular formula, molecular weight, CAS registry number and/or SDBS number, atomic numbers and by spectral bands from other techniques. The IR spectra are presented as transmittance spectra. Together with the spectrum come the compound name, molecular formula, SDBS number, method description (liquid film, KBr disc) and the table with the wavenumbers of the bands.

FT-IR Spectra at University of Tartu Testing Centre

This is a collection[19] of FT-IR spectra of various paint and coating materials that have been scanned at the University of Tartu. The spectra were acquired over the last few years in the course of various projects on historic, industrial and construction paints and coatings. Many individuals and institutions from the art conservation community and paint industry in Estonia have donated their painting materials (pigments, binders, fillers) and samples. Thanks to their continuing contributions, this collection of FT-IR spectra is gradually getting larger.

This collection of infrared spectra is specifically targeted to conservation professionals and conservation scientists. It contains two large sections: Pigments and Fillers, and Binders. The sections are divided into subgroups based on the pigment colour or the binder type (for example oils and waxes). Both sections have a related compounds subsection. The collection, which currently contains altogether 113 spectra (57 binders, 56 pigments/fillers), is updated on a regular basis.

Unlike many other spectral collections, this collection also presents spectra of some aged materials, currently limited to linseed oil aged in the presence of different pigments. The future plan is to significantly broaden the selection of aged materials, as this is of key importance in materials identification.

One of the advantages of this collection is that the spectra are accompanied by background information. Almost every IR spectrum has a short description of the material's physical and chemical properties; for example, chemical formula, colour and physical properties such as solubility and melting point. The historic background, very important for materials identification, is also given in most cases.

Liquid samples have been measured using the liquid film method, and solid samples have been measured using the KBr disc method with a resolution of 4 cm^{-1} and a spectral range of 400-4,000 cm^{-1}. All spectra are transmittance spectra. A drawback of this collection is the low quality of some of the spectra, resulting from the use of a low-end spectrometer.

The NIST Webbook

The National Institute of Standards and Technology (NIST) Webbook[20] is a very powerful, free-of-charge online database containing much physicochemical data. Infrared spectra are available for over 16,000 compounds, though unfortunately, these spectra are mostly of relatively simple organic compounds with a few spectra of materials and inorganic compounds. This is the only (although serious) drawback to this excellent database.

All the compounds data on the webpage are from collections retained by the NIST Standard Reference Data Program and outside supporters. The data are available in tabular form and also many types of data can be displayed with a graphic display.

The NIST Webbook has a very powerful search system with two search options: "General Searches" and "Physical Property Based Searches". From the conservation viewpoint, it is useful to search by the name, formula, structure and CAS registry number.

Infrared Spectra Study Booklet at Iowa State University

This useful, although small, student booklet[21] contains spectra of 33 inorganic materials and seven organic compounds. Especially useful are the spectra of inorganic salts, which are not easy to find in other databases. Many of the spectra were collected using the ATR accessory and some were collected in the transmission mode. The wavenumber range of the spectra is 4,000 – 600 cm^{-1}.

IR Spectra at Sigma-Aldrich

The chemical retail company Sigma-Aldrich Inc has a web-based product catalogue[22] that, among other things, also provides various spectra including IR, for many of the chemicals it sells. As the product line of Sigma-Aldrich is very extensive, the number of spectra that can be obtained is also large, although IR spectra are not available for all chemicals that Sigma-Aldrich sells. It is possible to search by product number, product name, keyword, molecular formula, CAS registry number, MDL[23] number, supplier number or substructure.

Results of a search bring up three categories: Products, Web Pages and Documents. Products can be divided into categories (i.e. analytical chemistry, drug discovery and organic chemistry), special grade (i.e. absolute, analytical and IR), manufacturer (i.e. Aldrich, Fluka, Riedel-de-Haën and Sigma), purity, formula weight, boiling point, melting point, pH value, physical form (i.e. aqueous, liquid and solid) and colour (white etc.).

For example, entering a compound into the search column makes it possible to obtain information about it. There are five categories: identifiers (including synonyms, molecular formula, molecular weight and CAS registry number), description (i.e. general description, actions and application note), properties (i.e. Merck and Beilstein reference) and safety information (including hazard codes, risk statements and safety statements). Entering the name of the product makes it possible to obtain a number of spectra including FTIR spectra.

The biggest drawback, from the point of view of conservation science is that, like many of the databases, the IR spectra are mostly limited to general organic compounds. There are very few spectra available for binding media and inorganic compounds. The complete FTIR spectra library, with over 11,000 spectra, can be purchased.

Articles and Dissertations Available Online

Several journals available on the World Wide Web publish articles about IR spectroscopy for conservation professionals. Some articles that are freely available and contain many spectra are reviewed here. These articles can be classified as mini-databases. Furthermore, in comparison with the spectral libraries and collections, these articles have the advantage of offering explanations and interpretations that greatly enhance the usefulness of the spectra. Two highly useful doctoral dissertations, also available online, are reviewed in this section. It should be noted that this is a highly selective list of articles and dissertations.

"Some applications of infrared spectroscopy in the examination of painting materials", by Richard Newman[24]

This article was published in the Journal of the American Institute for Conservation (JAIC)[25], which has published many other worthwhile papers on this topic that cannot be covered here. This particular article is an early work in the field outlining the use of IR spectroscopy in conservation science. The possibilities for the use of IR spectroscopy are explored and many examples are given. The paper contains 38 IR spectra of various materials used in paint formulations, including chrome green, green earth, chromium oxide and viridian. Spectra of several of the materials, for example the chromium-containing pigments, are hard to find elsewhere. Another very useful part of this paper is the short theoretical introduction into IR spectra of polyatomic ions (for example carbonate, sulfate and chromate). Such an introduction is missing from most textbooks on infrared spectroscopy that are usually strongly biased towards organic compounds.

"Fourier transform infrared spectral analysis of natural resins used in furniture finishes", by Michele Derrick[26]

This paper describes the capabilities and limitations of FTIR spectroscopy for the identification of natural resins used in historic furniture finishes. The five natural resins most often used, shellac, sandarac, mastic, copal and rosin, were analysed with infrared spectroscopy individually and as components in a mixture. The paper contains, in total, 10 IR spectra, mostly of natural resin. This paper is included because it gives the IR spectra of all of the important natural resins that conservators may use or encounter, thereby enabling comparison of such spectra.

"The identification of pigments in paper coatings by infrared spectroscopy", by Sharon D. Wightman, Alison Murray and Herbert F. Shurvell[27]

This paper, published in the Internet Journal of Vibrational Spectroscopy[28], discusses the use of infrared transmission measurements to identify the components of coatings on paper. Samples were taken from the following papers: bond typing paper, magazine paper, wallpaper, art stock, gift wrap, a post card, and printed catalogue papers. The age of the papers ranged from 100+ years to 15 years (late 19th century to the 1990s). The reference spectra were taken for seven common pigments, five protein binders, four different cellulose samples and four starches. The paper contains altogether 38 IR spectra, including reference spectra and coated paper sample spectra. Tables list the important IR absorption wavenumbers (cm^{-1}) of the materials and give short explanations of the spectral features. All the spectra in this article can be used for reference in the identification of pigments, coating materials and different papers.

"Analytical chemical studies on traditional linseed oil paints", by Jorrit Dirk Jan van den Berg[29]

This doctoral dissertation written within the framework of the MOLART project[30] sets out to clarify the chemistry of oil paint systems at different stages of ageing by examining the processes of chemical drying of oil and oil paint auto-oxidation and photo-oxidation. The effects of additions of inorganic or organic pigments to the oil are analyzed and the chemical composition of the mixture of oil and pigments after ageing is observed. Various analytical methods were used for the examination of the formation of degradation products and cross-linking associated with the ageing process. One of the analytical techniques was FTIR spectroscopy.

This doctoral work deals with two IR spectra: freshly pressed linseed oil and a linseed oil sample heated in an ageing process to an end temperature of 300 ºC. In addition to the IR spectra generated by these samples, there is a table including the wavenumbers (cm^{-1}) for the bands and their interpretations (assignments of structural fragments to the absorption bands). In spite of the small number of IR spectra with which it deals, this doctoral dissertation is worth mentioning here because the accompanying discussion presents a thorough theoretical study of the curing, ageing and degradation of linseed oil. This provides very useful background information for spectral interpretation of aged linseed oil.

"Microspectroscopic analysis of traditional oil paint", by Jaap van der Weerd[31]

This doctoral dissertation also written as part of the MOLART project,[30] focuses on the development of spectroscopic imaging techniques for paint research. Several paint samples from ageing paintings were examined by different micro-analytical and imaging techniques, including light microscopy, FTIR and FTIR-imaging.

This thesis can be broken down under the following headings: development of different imaging techniques and sample preparation methods; the characterization of naturally aged paints; and the investigation of samples from paintings using several techniques. There are descriptions of the processes taking place during oil drying. The initial reactions in a drying oil were observed by FTIR spectroscopy.

In this study there are 83 IR spectra in total of which 44 are of thin paint layers taken with FTIR or FTIR-imaging techniques and 39 examine the effects of various pigments on the ageing of linseed oil using FTIR spectroscopy.

Discussion

A number of excellent commercial IR databases are available; however, the presence of conservation-related materials is in many cases, limited or, as in the case of aged materials, non-existent. Moreover, the databases are quite costly. None of the freely available IR spectral databases described above is ideal in that none satisfies all the potential requirements of conservators. Some, focused more on cultural materials, provide relevant spectra with a good range of samples (naturally aged, different sources etc.). Taken as a whole, these spectral resources form a very powerful "virtual database", the most important properties of which are:

- A wide selection of IR spectra of conservation-related materials, including multiple spectra of the same material (for example, from different institutions and geographic locations).
- Availability of spectra of aged materials, a critical feature since most of the artifacts that conservators examine or treat are old.
- Availability of spectra of real materials (mixtures in most cases as materials under study are not usually pure) and accompanying discussions and explanations. These can be found in the on-line articles and dissertations. Interpretation of IR spectra remains by and large an art, where experience and knowledge play an important role.

Altogether several tens of thousand of IR spectra are freely available on the World Wide Web (50,000 at SDBS alone). It is difficult to estimate how many of them are conservation-relevant, however. The current version of the largest conservation-relevant database, IRUG, contains over 1,250 spectra, added to which are at least several hundred spectra from other sources, giving a possible total of between 1,400 and 1,800 spectra with direct relevance to conservation. There are, of course, many overlaps among the different sources, but as explained above, this duplication can be useful in the interpretation of specific classes of spectra.

From the available conservation-related IR spectral collections, the very well organized IRUG database can be singled out as by far the most voluminous.

Conclusion

IR spectroscopy is one of the most popular analytical tools in use by conservators today. This cost-effective method can be used to identify most of the organic and some inorganic compounds; however, interpretation can be done only by comparison to reference spectra. This review demonstrates that much work can be done using the free spectral resources available on the World Wide Web. Eleven free online sources of reference infrared spectra have been described, of which more than half are of direct interest for conservation scientists. Of the many tens of thousands of reference infrared spectra freely available on the World Wide Web, it is estimated that between 1,400 and 1,800 are directly relevant for conservation science.

Acknowledgements

Parts of this work were supported by the Estonian Science Foundation grant 5475, awarded to the University of Tartu for the time period of 2003-2006 for the purpose of developing procedures in areas of chemical analysis.

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Note: all web sites were accessed as of September 2005.

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2. *The Internet Journal of Vibrational Spectroscopy*, vol. 2, edition 4, 2004, Special Issue on microscopic vibrational spectroscopy. Available at http://www.ijvs.com/volume2/edition4/section1.html.

3. Traditionally most of the infrared spectra were scanned as transmittance or absorbance spectra (the radiation was passed through a thin layer of material). Contemporary IR spectroscopy is gradually moving away from such measurements and towards the reflectance techniques, such as ATR (Attenuated Total Reflectance) and DR (Diffuse Reflectance). These measurements are simpler and often (especially ATR) give high quality spectra. Details can be found in references 1 and 5.

4. Gillie, J. Kevin, Hochlowski, Jill, and Arbuckle-Keil, Georgia A., "Infrared Spectroscopy," *Anal. Chem.* vol. 72, no. 12, 2000, pp. 71 - 80.

5. Absorbance and transmittance are interconnected by a simple equation $A = \log(100/T)$, where absorbance A is measured in absorbance units and transmittance T is measured in percentages.

6. It must be clearly stated here that most of the free IR Spectral Library sites explicitly preclude the use of the spectra for commercial purposes. Use is permitted only for teaching and research. Detailed conditions of use vary from site to site.

7. Bio-Rad Informatics/Sadtler's "KnowItAll/HaveItAll" products on the Web at http://www.knowitall.com.

8. Bio-Rad Sadtler sells this service to academic institutions for approximately 1,700 euros (around CDN$2,400) for a period of one year.

9. FTIRsearch.com on the Web available at http://www.ftirsearch.com/.

10. Raman spectroscopy is a spectroscopic tool that gives information similar to IR spectroscopy but is based on completely different physical principles and different instrumentation. Although Raman spectra and IR spectra cannot be interpreted interchangeably, these two techniques can greatly enhance each other's capabilities when used in combination. Further details can be found in Skoog, Douglas A., Holler, F. James, Nieman, Timothy A., *Principles of Instrumental Analysis*, 5th edition, (Philadelphia: Saundes College Publishing, 1998), 832 pages.

11. The price of 100 credits is US$100 (CDN$118), the price for 2,500 credits is US$2,000 (CDN$2,364).

12. FDM Electronic Handbook of FTIR Spectra on the Web available at http://www.fdmspectra.com/fdm_ehb.htm.

13. For example the 310 spectra of mineral and inorganics cost US$695 (CDN$822) but the complete IR spectra collection (11,240 spectra) can be bought at a cost of US$2,995 (CDN$3,540).

14. S. T. Japan Spectral Library on the Web at http://www.stjapan.de/.

15. For example the Dyes, Pigments and Stains Library with 845 spectra costs around 1,200 euros (CDN$1,705); Polymer and Polymer Additives Library with 1,124 spectra costs around 1,600 euros (CDN$2,273).

16. IRUG – Infrared and Raman Users Group Spectral Database available at http://www.irug.org/.

17. Wavenumbers, measured in cm^{-1}, are the energy units generally used in infrared spectroscopy.

18. SDBS - Integrated Spectral Data Base System for Organic Compounds. National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan. Database available at http://www.aist.go.jp/RIODB/SDBS/menu-e.html.

19. FT-IR Spectra of Binders and Colorants. University of Tartu, Testing Centre. The spectra are available at http://www.ut.ee/katsekoda/IR_Spectra/.

20. NIST Chemistry Webbook. National Institute of Standards and Technology. Available at http://webbook.nist.gov/.

21. Infrared Spectra Study Booklet at Iowa State University. Available at http://avogadro.chem.iastate.edu/Infrared/IR_Booklet.pdf.

22. Sigma-Aldrich Catalogue on the Web available at http://www.sigmaaldrich.com/.

23. The abbreviation MDL stands for a company Molecular Design Limited which provides scientific databases. This company is now part of the Elsevier group.

24. Newman, Richard, "Some Applications of Infrared Spectroscopy in the Examination of Painting Materials", *Journal of the American Institute for Conservation*, vol. 19, no. 1, 1979, pp. 42-62. Available online at http://aic.stanford.edu/jaic/articles/jaic19-01-006_indx.html.

25. *Journal of the American Institute for Conservation* on the Web available at http://aic.stanford.edu/jaic/.

26. Derrick, Michele, "Fourier Transform Infrared Spectral Analysis of Natural Resins Used in Furniture Finishes", *Journal of the American Institute for Conservation*, vol. 28, no. 1, 1989, pp. 43-56. Available online at http://aic.stanford.edu/jaic/articles/jaic28-01-004.html.

27. Wightman, Sharon D., Murray, Alison, Shurvell, Herbert F., "The Identification of Pigments in Paper Coatings by Infrared Spectroscopy", *The Internet Journal of Vibrational Spectroscopy,* vol. 3, edition 3, section 1. Available online at http://www.ijvs.com/volume3/edition3/section1.html.

28. *The Internet Journal of Vibrational Spectroscopy* on the Web available at http://www.ijvs.com.

29. van den Berg, Jorrit Dirk Jan, *Analytical Chemical Studies on Traditional Linseed Oil Paints* (Amsterdam: Amsterdam University, 2002). Ph.D. Thesis (advisor: Prof. Dr. Jaap J. Boon), FOM-Institute for Atomic and Molecular Physics (AMOLF), in the framework of the MOLART project. Available at http://www.amolf.nl/publications/theses/berg/index.html?berg.html.

30. The MOLART Project: Molecular Aspects of Ageing in Painted Works of Art. The final report is available at http://www.amolf.nl/research/biomacromolecular_mass_spectrometry/molart/molart.html.

31. van der Weerd, Jaap, *Microspectroscopic Analysis of Traditional Oil Paint* (Amsterdam: Amsterdam University, 2002), Ph.D. Thesis (advisors: Prof. Dr. Jaap. J. Boon, Prof. Dr. Heeren, R.M.A.), FOM-Institute for Atomic and Molecular Physics (AMOLF), in the framework of the MOLART project. Available at http://www.amolf.nl/publications/theses/weerd/index.html?weerd.html.