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Abstracts

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Derivatisation strategies for micro-FTIR and chemical imaging FTIR-FPA - fluorination reagents to discriminate spectral interferences in paint samples

Stefan Zumbühl, Nadim C. Scherrer

INTRODUCTION

Fourier Transform Infrared Spectroscopy (FTIR) is a well-established analytical technique for paint samples and materials in conservation science. With the development of Focal Plane Array (FPA) detectors in the past 15 years, FTIR spectroscopic imaging has emerged as a powerful tool for chemical imaging [Salzer 2009]. ATR (attenuated total reflectance) technology allows the localisation and identification of organic and inorganic compounds in micro-samples at higher spatial resolution, beyond the optical diffraction limit. There are, however, limitations to the technique when analysing chemically complex multi-component materials. Paints are complex systems containing organic binding media, colorants, mineral fillers and several system- or production-relevant additives and ageing products. As most of these compounds are infrared-active, spectral interferences hinder the full characterisation of the binding media, with minor components remaining undetected. Thus it is of interest to discriminate overlapping signals and achieve signal enhancements on superimposed compounds. For standard analytical procedures using FTIR-FPA imaging, the signal separation in multi-compound systems is essential to derive chemical maps, as signal integration is only possible on isolated spectral bands.

THEORY OF DERIVATISATION

In order to improve the selectivity of the infrared spectroscopy, two preparation techniques were used to eliminate signal interferences in paint samples. Either the organic components are separated by micro-extractions from the insoluble solids, or the filler is chemically converted into a non-IR-active compound [Jönnson 2004]. The second method is largely restricted to the elimination of calcium carbonate with dilute hydrochloric acid. Both methods are destructive and have major drawbacks as they are only applicable to micro-samples, and they lead to the loss of the morphological context of the sample material. For these reasons they are not suited to FTIR-FPA imaging. Thus, spectral discrimination in solids by selective chemical modification of functional groups in gas phase delivers an interesting alternative to the above-mentioned approaches.

Different derivatisation concepts rely on either selective shifting of IR-bands resulting in splitting of overlapping bands, or by eliminating interfering signals. These effects are achieved by conversion of chemical bonds, since IR absorption and the resulting vibrational frequencies are dependent on bond force constant, atomic masses and molecular geometry [Socrates 1998]. The mid-infrared absorption of an individual bond is mainly dependant on the change in dipole moment, the steric orientation of the functional group within a molecule, as well as its sensitivity to neighbouring group effects [Stuart 2004]. In inorganic materials, the crystalline structure has a decisive influence on the IR-activity of an inorganic material [Farmer 1974]. If the vibration has zero change in its dipole moment, what is true for cubic crystals, it does not absorb IR light. Contrary to highly symmetric crystals, all minerals containing polyatomic ions exhibit strong IR signals, since the anions themselves have several internal vibration modes [Farmer 1974]. Derivatisation techniques aim at modifying IR-absorption selectively by characteristic alteration of the binding modes. The aim of derivatisation is to achieve a controlled, characteristic and reproducible functional group modification. Thus, based on the theory of infrared spectroscopy we can deduct 4 principle strategies to eliminate spectral

interferences from organic and inorganic materials. The following principles are of practical relevance in this context: I) Single atom substitution within functional groups, II) Substitution of entire functional groups, III) Modification of the neighbouring groups of an IR absorbing bond, and IV) Modification of the crystal structure by ionic exchange.

FLUORINATION REACTIONS

Within this context of infrared spectroscopy, derivatisation of organic and inorganic materials by fluorination reactions is of interest, since various exchange reactions are possible due to the small mass of the fluorine. Furthermore, organic fluorine compounds show characteristic and narrow IR bands [Socrates 1998], which are specifically suited to FTIR analysis. The fluorination of an organic molecule can influence both, the absorption of the hydrocarbon backbone as well as of the functional groups. Due to the strong coupling of C-C and C-F stretching, fluorinated compounds can show specific absorption of the halogenated group [Socrates 1998]. Adjacent atoms, such as halogens, furthermore increase the intensity of weakly absorbing vibrations such as CH wagging, twisting and bending [Vandeberg 1980]. In functional groups the change in position of a vibration mode can be attributed to the mass effect, but is also due to the change in electron distribution, brought about by the substituted atom. It has been observed, for example, that inductive and resonance effects have the greatest influence on the shift in the carbonyl stretching frequencies [Vandeberg 1980].

There is a wide range of materials being modified by fluorination in industrial applications and there are a great number of specific reagents applied in different processes [Baasner 1999; Furin 1991]. In practice, however, the options to apply selective fluorination in combination with a spectroscopic technique are strongly limited since most fluorination reactants are either liquids or, their reaction proceeds in solution [Paquette 2007; Furin 1991]. Of the gaseous reagents, elemental Fluorine F_2, anhydrous hydrogen fluoride HF, and sulphur tetrafluoride SF_4 play an important role. To achieve the chemical modification of the hydrocarbon backbone, elemental fluorine F_2 is often used in industrial applications. Besides applying it for the total substitution of hydrogen, it is also used for the selective replacement of specific hydrogens in aliphatic and aromatic molecules, and for the addition of fluorine to various types of double bonds [Baasner et al. 1999]. Among these, anhydrous hydrogen fluoride HF is the currently most widely used industrial fluorinating agent for selective processes. But it has a major drawback, however, namely a number of secondary reactions that are due to its high acidity [Baasner et al. 1999]. Therefore, the weakly acidic sulfur tetrafluoride SF_4 attracts more practical interest for the analysis of paint samples and materials in conservation science. It is a corrosive gas at standard temperature and humidity conditions, forms hydrogen fluoride HF upon exposure to moisture (Reaction 1) and, it is a precursor to many organofluorine compounds. It converts hydroxyl, carbonyl, and carboxylic acid groups into mono-, di-, and trifluorinated functionalities, respectively [Wang 2004]. For each class of functional groups, different reactions take place under variable reaction conditions [Paquette 2007; Wang, 2004]. This reagent was recently tested for practical application to investigate oil, alkyde and tempera paint samples [Zumbühl 2014].

DERIVATISATION REACTIONS IN PAINT MATERIALS

The initial application of sulfur tetrafluorid SF_4 to paint samples has revealed different selective derivatisation reactions of *I) organic components, II) various organometallics* and *III) inorganic materials*, which may be exploited by IR spectroscopy. The application of this technique enabled the chemical characterisation and localisation of the different functional groups with clear signal discrimination:

I) Derivatisation of organic materials:

The gaseous sulfur tetrafluoride SF_4 treatment was chosen to achieve the distinction of carbonyl bands from ketones and carboxylic acids and esters, which is one of the main difficulties identifying material mixtures made from organic compounds and characterising of the oxidation state of a material. The principle of this technique is the selective conversion of carboxylic acids R(O)OH into an acyl fluoride R(O)F (Reaction 2) [Wilhelm 1994]:

(1) $SF_4 + 2\ H_2O \rightarrow SO_2 + 4\ HF$
(2) $C(O)OH + HF \rightarrow C(O)F + H_2O.$

Since fluorine has a high electronegativity, the highly inductive effect of this neighboring atom raises the frequency of the ν(C=O) vibrational mode of the modified acid carbonyl group. This derivatisation product shows characteristic IR vibrations at 1841cm^{-1} (Wilhelm, 1994), while ketones ν(C=O) at ≈1720cm^{-1} and ester groups ν(C=O) at ≈1740cm^{-1} remain intact. IR spectra after SF_4 treatment of such samples show the characteristic splitting of the carbonyl band, allowing the distinction of the individual functional groups **(Figure 1)**. Moreover, the elimination of the carboxylic νO-H signal makes it possible to detect alcoholic hydroxyls selectively.

II) Derivatisation of organometallic materials:

In the field of art conservation science, the combination of IR absorption of the organic, organometallic and inorganic compounds make it rather difficult to study the binder components in curing oil paint. Research on old oil paint samples has shown that it is possible to derivatise not only carboxylic acids, but also their salts R(O)OM into an acyl fluoride R(O)F:

(3) $C(O)OM + HF \rightarrow C(O)F + MOH$
$MOH + HF \rightarrow MF + H_2O.$

This is of interest for the investigation of oil-based paints. Following derivatisation treatment, the broad signals of carboxylates at around ≈1600cm^{-1} ν_a ($C(O)O^-$) [s], ≈1450cm^{-1} ν_s ($C(O)O^-$) [m-s] and ≈850cm^{-1} sci ($C(O)O^-$) [m] [Socrates, 1998] are no longer present **(Figure 2)**. The conversion of the strongly IR-absorbing ageing products such as zinc or lead soaps is of great interest, since it allows to explore the different superimposed C-H deformation and wagging vibrations [Zumbühl 2014].

III) Derivatisation of inorganic materials:

The conversion reaction of inorganic compounds is of particular interest in this context in order to eliminate the broad overlapping bands of some strongly IR-absorbing mineral fillers or pigments, as some have shown to be transformed into a non-IR active components. So far this reaction has only been investigated in detail for carbonates such as calcite $CaCO_3$, cerussite $2PbCO_3$ and hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$. The pigment conversion of basic lead carbonate is of great interest, as it was very popular and widely applied in paint manufacturing. The strong and broad ν_3 carbonate bands of the CO_3^{-2} ion at ≈1410cm^{-1} generally strongly limit FTIR analyses on binding media. Upon derivatisation using SF_4, all carbonate absorption bands are eliminated **(Figure 2b)**, since the pigment is converted into the non-IR active cubic lead(II)fluoride β-PbF_2 [Zumbühl 2014]:

(4) $Pb(OH)_2 + 2\ HF \rightarrow PbF_2 + 2\ H_2O$
$PbCO_3 + 2\ HF \rightarrow PbF_2 + H_2O + CO_2.$

DISCUSSION AND CONCLUSION

A major drawback of infrared spectroscopy is the poor selectivity in complex material systems due to signal interferences of different functional groups within similar spectral ranges, causing the minor components to remain undetected. This is of great limitation, in particular to the study of binding media analysis on artwork. A pre-treatment with gaseous sulfur tetrafluoride SF_4 to derivatise certain compounds substantially increases the selectivity of the FTIR technique by eliminating signal overlaps. As example this reagent was recently applied to investigate the protein content in tempera paint [Zumbühl 2014] (Figure 3). Furthermore, signal discrimination is also of interest for chemical imaging using the focal plane array technology FTIR-FPA. Besides the derivatisation of micro-samples, this pre-treatment can also be applied to polished cross-sections or surfaces. The technique allows research on the interrelationships of such complex material systems within the original stratigraphic structure [Zumbühl 2014] (Figure 1b,3b). The application of the SF_4 derivatisation technique on embedded and polished samples shows that the extent of the reaction with gaseous SF_4 is only superficial, yet deep enough for successful attenuated total reflectance ATR measurements. The IR penetration depth using ATR technology in organic layers using a germanium crystal is in the range of 0.2-0.7 µm [Salzer 2009], meaning that a reaction depth of 1µm during derivatisation is sufficient for the method to work successfully. The standard reaction time of 24h was sufficient to achieve an ubiquitous and homogenous derivatisation across the polished surface in all cases. The reaction products were found to remain stable for several weeks and can easily be removed by repolishing. It can be concluded, that a derivatisation pre-treatment with reactive fluorine gases has great potential to increase the selectivity of infrared spectroscopy in conservation science. The applicability of the technique in combination with 2D FTIR-FPA imaging at a spatial resolution of 1-1.5µm opens a new level of information when researching aged paint layer stratigraphies.

Literature:

Baasner, B., H. Hagemann, J.C. Tatlow, Organo-Fluorine Compounds, Thieme Verlag, Stuttgart, 1999.

Farmer, V.C., The Infrared Spectra of Minerals, Mineralogical Society London, 1974.

Furin, G.G., Synthesis Aspects of Fluorination of Organic Compounds, Harwood Academic Publishers, Chur, 1991.

Jönnson, J., T. Learner, Separation of Acryl Paint Components and Their Identification with FTIR Spectroscopy, in: M. Picollo, (Ed), The Sixth Infrared and Raman Users Group Conference IRUG6, Florence Italy, March 29 – April 1, 2004.

Paquette, L.A., Handbook of Reagents for Organic Synthesis: Fluorine-Containing Reagents, John Wiley & Sons Ltd., Chichester, 2007.

Salzer, R., H.W. Siesler, Infrared and Raman Spectroscopic Imaging, Wiley-VCH, Weinheim, 2009.

Socrates, G., Infrared Characteristic Group Frequencies: Tables and Charts Wiley Chichester, 1998.

Stuart, B.H., Infrared spectroscopy: fundamentals and applications Wiley, Chichester, 2004.

Vandeberg, J.T (Ed.), An Infrared Spectroscopy Atlas for the Coating Industry, The Infrared Spectroscopy Committee of the Chicago Society for Coatings Technology, Federation of Societies for Coating Technology, Philadelphia, 1980.

Wang, C.-L.J., Fluorination by Sulfur Tetrafluoride, John Wiley & Sons Inc., 2004.

Wilhelm, C., J.-L. Gardette, Infrared Identification of Carboxylic Acids Formed in Polymer Photooxidation, Journal of Applied Polymer Science 51(1994) 1411-1420.

Zumbühl, S., N.C. Scherrer, U. Eggenberger, Derivatization Technique to Increase the Spectral Selectivity of Two-Dimensional (2D) Fourier Transform Infrared Focal Plane Array (FT-IR FPA) Imaging: Analysis of Binder Composition in Aged Oil and Tempera Paint, Applied Spectroscopy 68(2014) 458-465.

Figures:

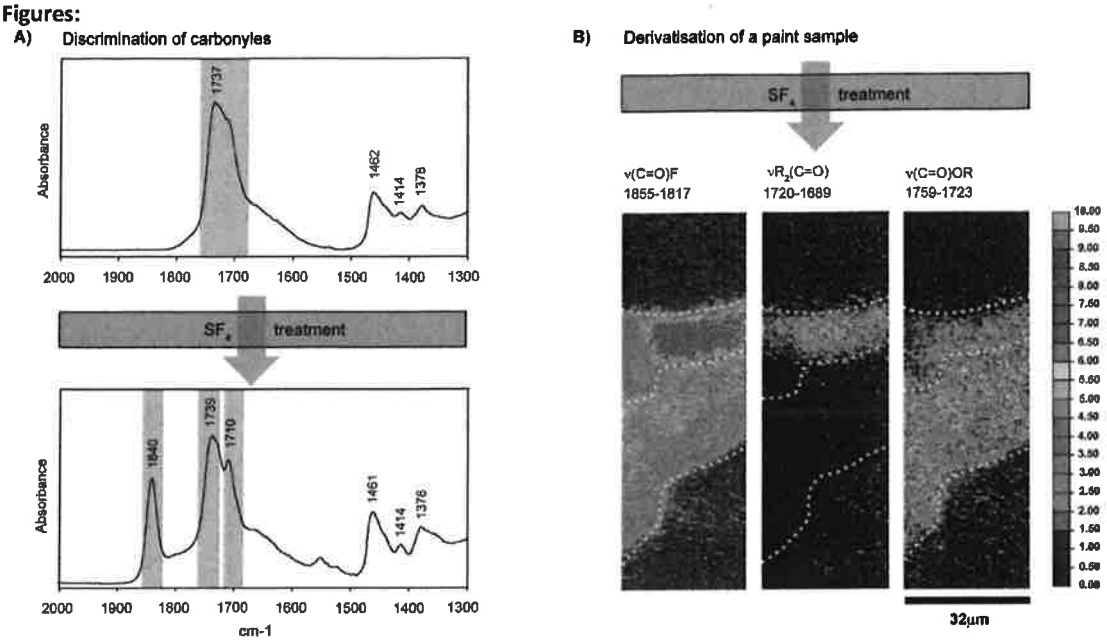

Figure 1 A) Micro-FTIR spectra before (upper) and after SF_4 treatment (lower). Focus is on the splitting of the carbonyl band upon SF4 treatment, which permits the distinction of acids (as acyl fluoride) ≈1740cm^{-1}, ketones ≈1710cm^{-1}, and esters ≈1740cm^{-1}. B) FTIR-FPA imaging on a cross-section: SF_4 derivatisation enables the localisation of the various carbonyls within very thin layers of about 10 Microns.

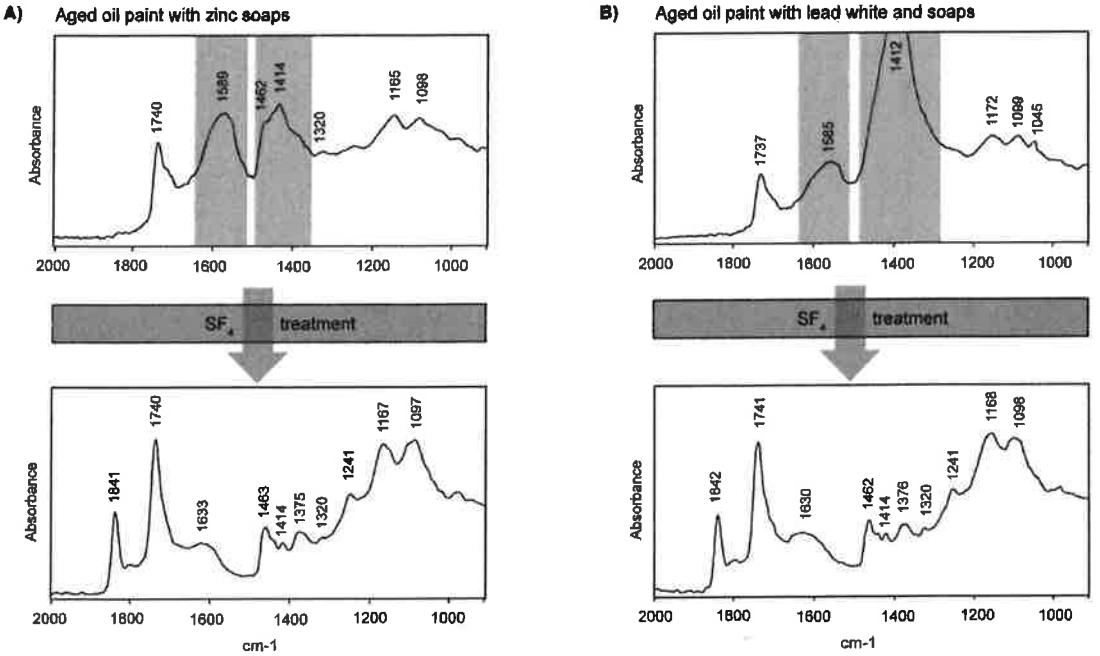

Figure 2 A) Derivatisation of 60-year old oil paint films containing zinc soaps (and zinc white), and B) a 60-year old oil paint film containing lead white and lead soaps (upper) and after SF_4 treatment (lower). After the elimination of the signals from the organometallic and inorganic compounds, the C-H signals at 1463cm^{-1}, 1414cm^{-1} and 1375cm^{-1} of the oil binder are uncovered.

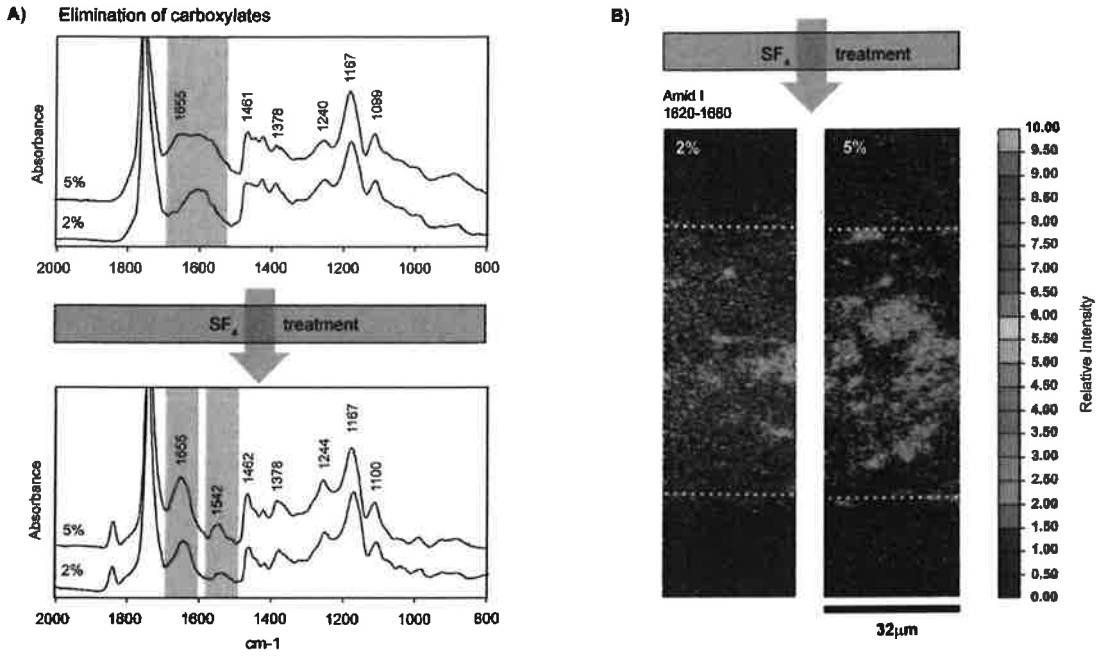

Figure 3 A) Micro FTIR: Derivatisation of tempera paint made of zinc white with variable protein content of 2% and 5% (protein/oil ratio) before (upper) and after (lower) derivatisation with SF_4. B) FTIR-FPA images: The SF_4 pre-treatment enables the localisation of the protein inclusions within a paint film. This is not possible without the elimination of the carboxylate signals in aged paint.