Derivatisation technique for enhanced FTIR-FPA imaging:

localisation of oxidative ageing products and additives in modern oil and tempera paint

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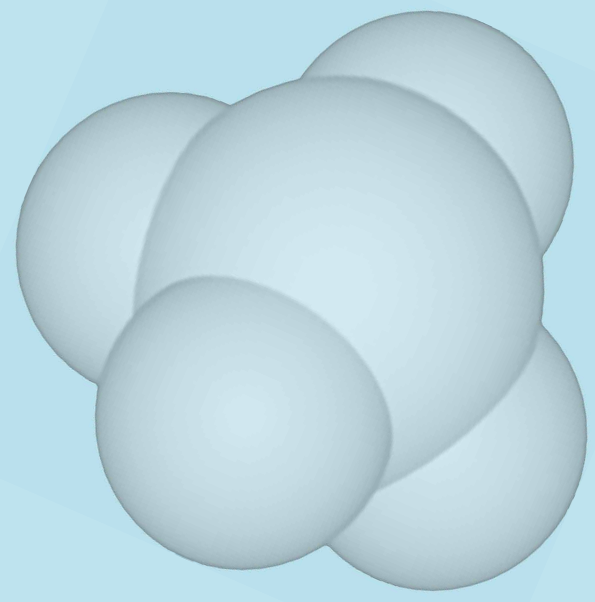

Introduction

The interpretation of standard infrared spectra (FTIR) on oil based paint samples often suffers from interfering bands of the different compounds, namely binder, oxidative ageing products, and pigments. The distinction of the ageing products such as ketone and carboxylic acid functional groups pose the next problem, as these interfere with the triglyceride esters of the oil. A sample preparation and derivatisation technique was thus developed with the aim to discriminate overlapping signals and achieve an enhancement on underlying compounds. The derivatisation treatment can be applied to both micro-samples and polished cross-sections. This sample pre-treatment step was performed in an all-teflon® reaction chamber. The treatment is surficial, homogenous across the surface, stable for several days, and can be removed by repolishing. In combination with FTIR-FPA imaging using the ATR technique it is possible to visualise the distribution of chemical ageing products across a paint cross-section at a spatial resolution of 1-1.5 microns.

Derivatisation using sulfur tetrafluoride

The highly reactive gas sulfur tetrafluoride SF_4 was used to selectively convert carboxylic acids C(O)OH and carboxylates C(O)OM into acyl fluoride C(O)F. This conversion product shows a specific νC(O)F absorption in the region around ≈1840cm^{-1} while ketone (≈1740cm^{-1}) and ester groups (≈1720cm^{-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 carbonyl containing functional groups formed during oxidative ageing of oil paint (**Fig. 1**). The elimination of the carboxylic O-H signal makes it possible to detect the hydroxyl groups selectively.

Furthermore, interference from some pigments such as the very strong ν_3 carbonate signal of lead white can be eliminated as well. The basic lead carbonate is converted into lead fluoride PbF_2 which is not active in the IR. With the removal of the νCO_3^{-2} vibrations (≈1400cm^{-1}) of the lead carbonate, typical patterns of δC-H-vibrations by the oil binder become visible (**Fig. 1**).

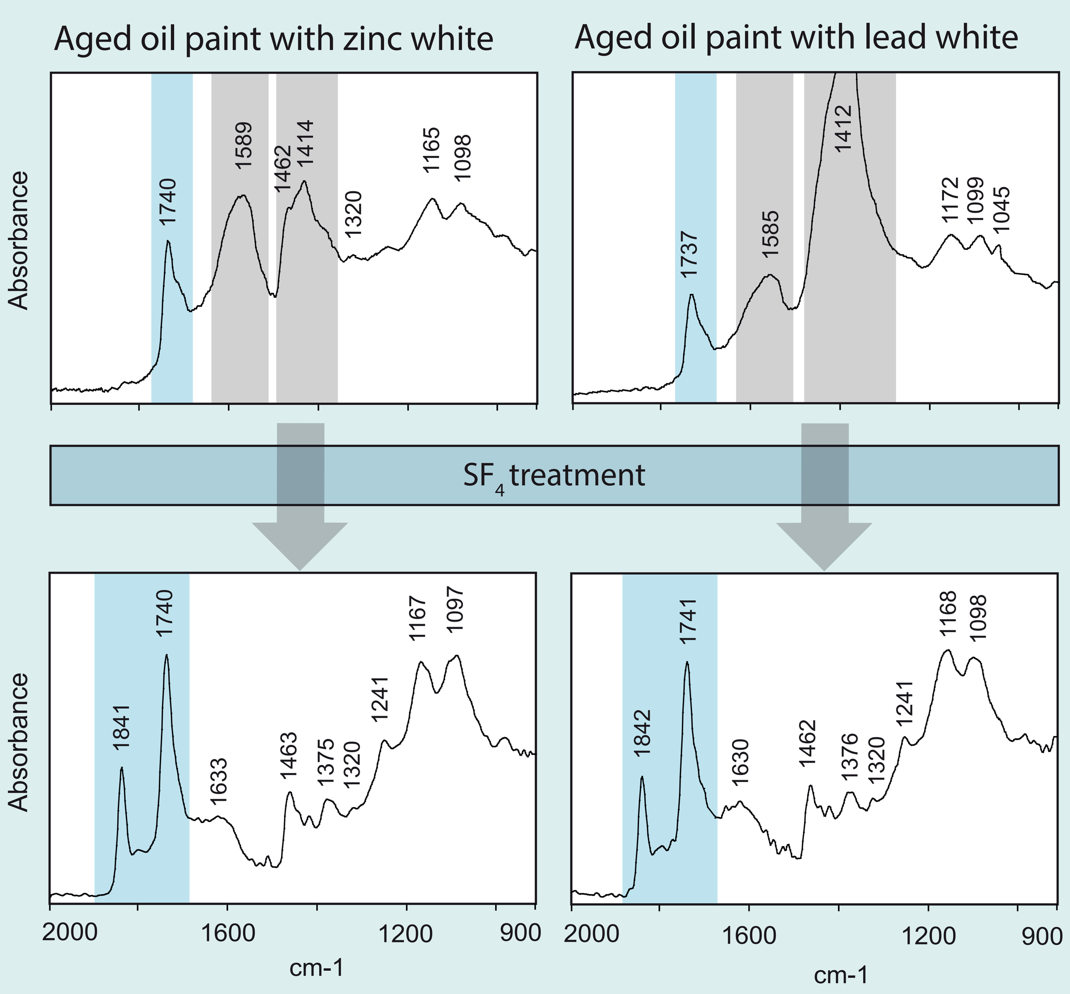

Fig. 1 Derivatisation of 60-year old oil paint films before (upper) and after SF_4 treatment (lower). Interference of the soaps and the pigments is eliminated (grey). The different carbonyl groups are now visible as separated bands (blue).

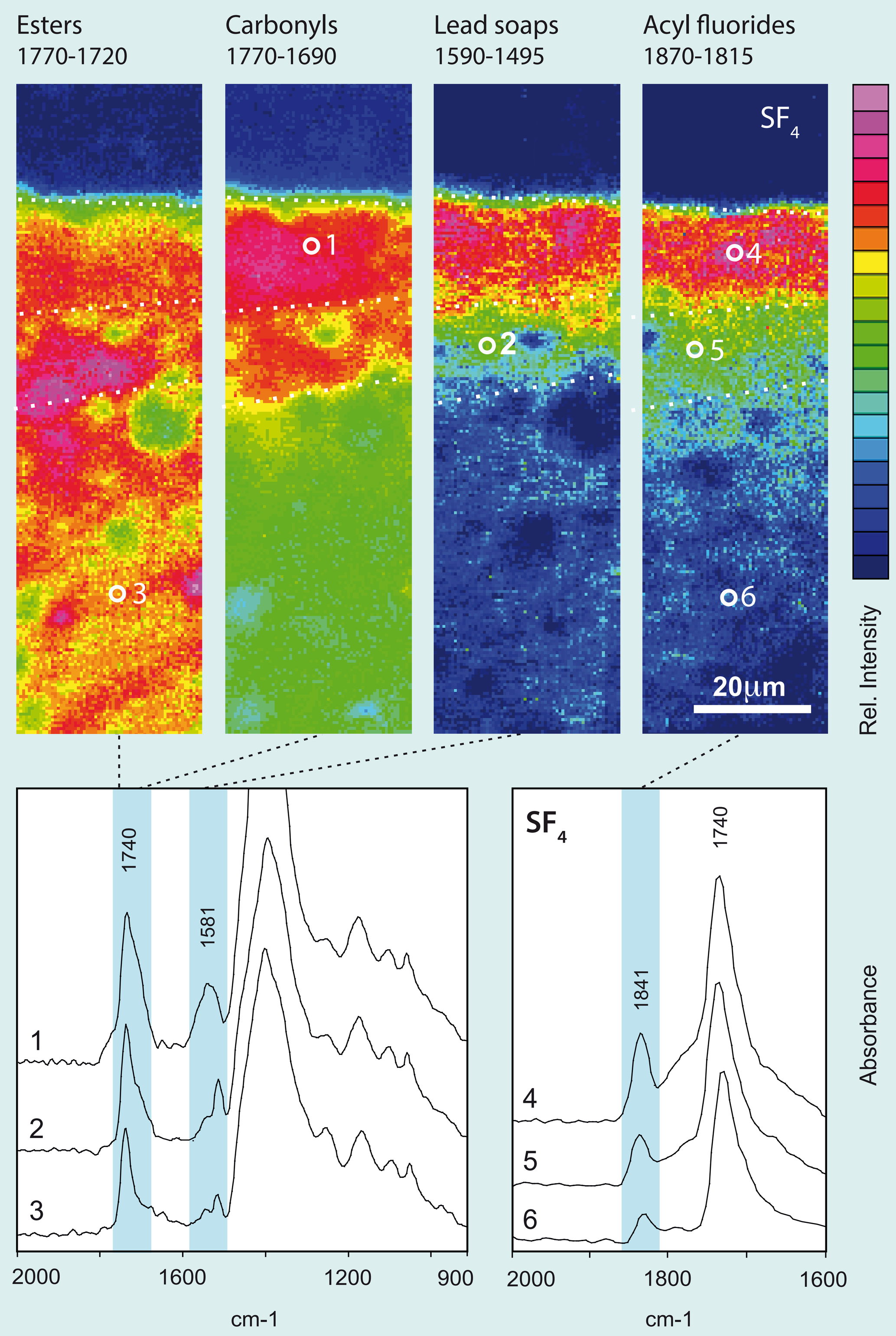

Fig. 2 Derivatisation of oil paint containing lead white. The FTIR-FPA imaging before and after treatment with SF_4 delivers information on the spatial distribution of the different oxidation and degradation products formed within a paint layer.

Application of the derivatisation technique

2D FTIR-FPA imaging on SF_4 treated crosssections permits to map the different functional groups of ageing products and their relative concentrations within a paint layer and thus delivers information on the drying and degradation process of modern oil paint (**Fig. 2**). With the help of this technique it is possible to gain information on the interrelation of the different chemical reaction pathways during the ageing of modern oil paint **[1]**.

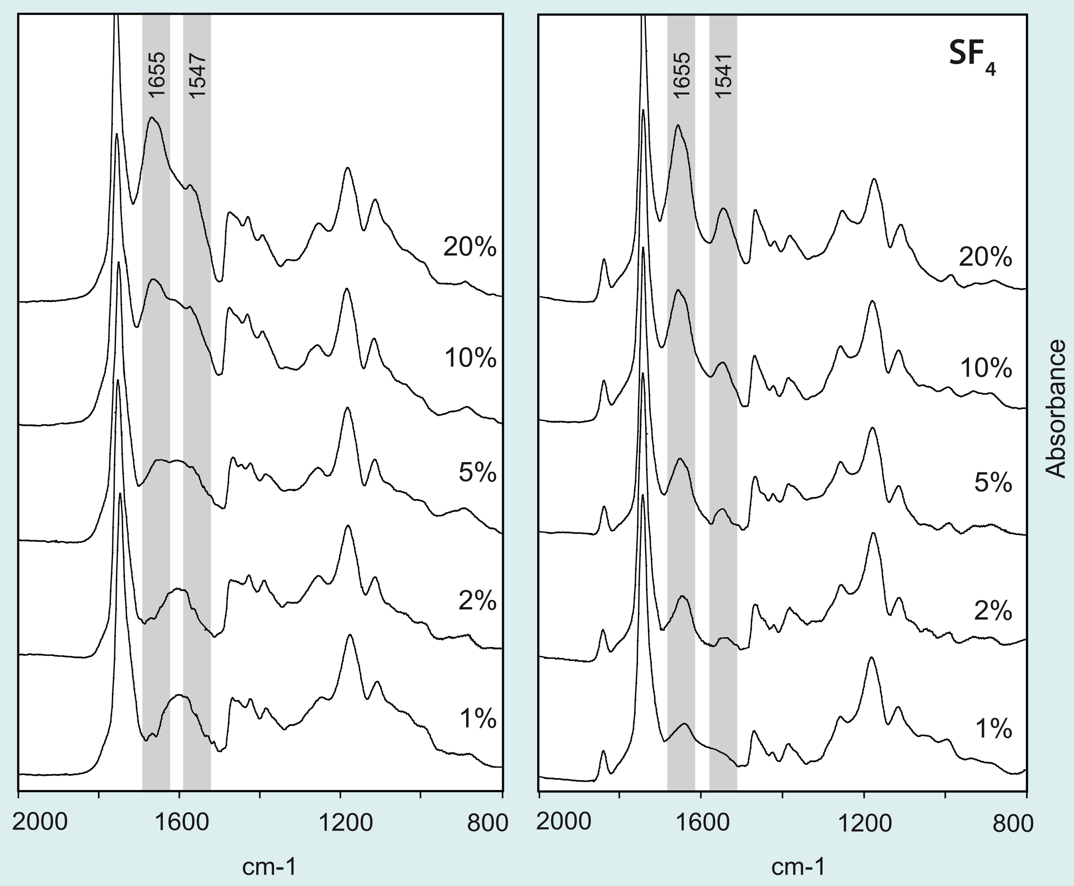

Fig. 3 Derivatisation of tempera paint containing zinc white with variable protein content (1-20%) before (left) and after (right) derivatsation with SF_4. After the elimination of the zinc soaps, the amide bands (grey) are clearly resolved.

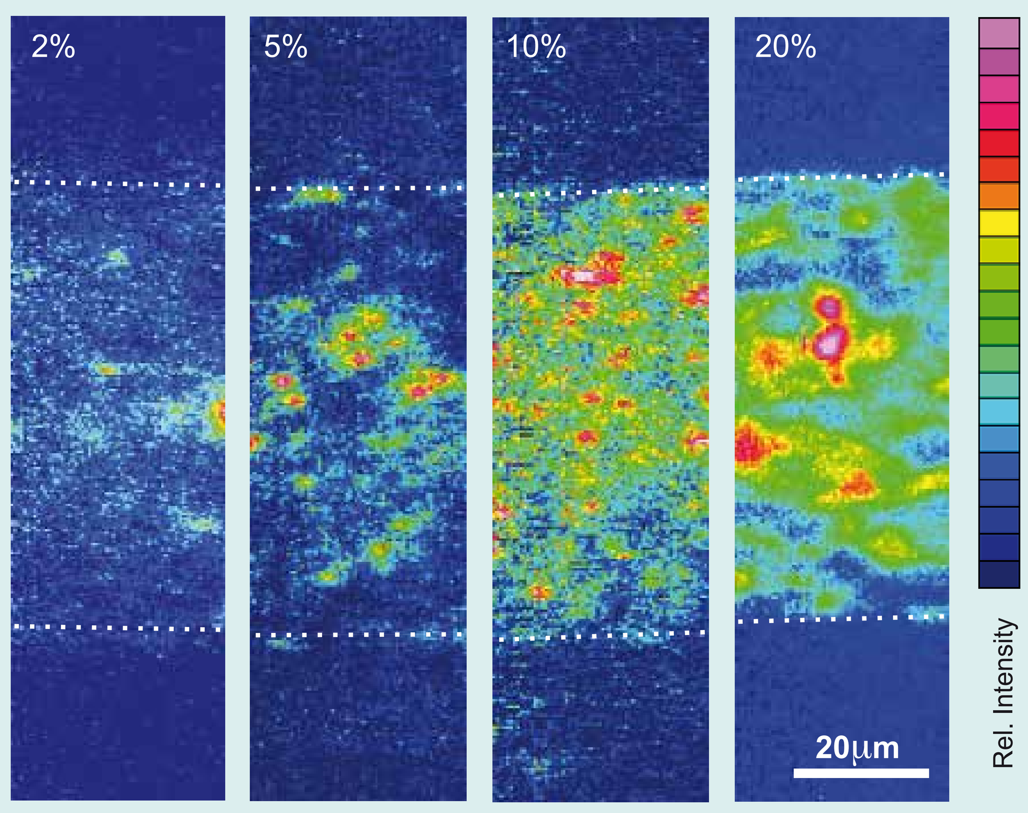

Fig. 4 FTIR-FPA imaging of the amide I concentration (1620-1680cm^{-1}) within a tempera paint sample. Pre-treatment using SF_4 made it possible to identify and localise proteinic compound within the paint layer.

Increasing the spectral selectivity of FTIR

The paint sample derivatisation is also used to increase the spectral specificity of the FTIR technique for the identification of modern tempera paint. The detection of small protein concentrations in oil-based systems is often strongly limited by signal interferences. In aged paint the broad bands of the carboxylate anion ν_a (COO^{2-}) at ≈1600cm^{-1} interfere with the protein bands amide I at ≈1650cm^{-1} and amide II at ≈ 1540cm^{-1}. The detection of the emulsifying component is thus limited to high protein concentrations. After the conversion of the carboxylate into an acyl fluoride, even small protein contents are detectable with FTIR (**Fig. 3**). Proteins within a tempera paint layer can thus be mapped at a spatial resolution of 1.5 microns applying FTIR-FPA imaging on SF_4 treated surfaces (**Fig. 4**).

Publication
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Reference **[1]** Zumbühl S., Scherrer N.C., Ferreira E.S.B., Hons S., Müller M., Kühnen R. and Navi P. (2011). Accelerated Ageing of Drying Oil Paint: An FTIR Study on the Chemical Alteration. Zeitschrift für Kunsttechnologie und Konservierung 25 (2) 139-151.

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