NOVEL MASS SPECTROMETRIC APPROACHES FOR THE ANALYSIS OF MODERN OIL PAINT MEDIA AND ORGANIC ADDITIVES IN PAINTINGS

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Main scientific topic: Chromatography & Mass spectrometry (GC, HPLC)
Preferred type of presentation: ORAL x POSTER ☐
I intend to submit a full paper to Analytical Bioanalytical Chemistry: YES x NO ☐

Introduction

Modern unvarnished oil paints in paintings show degradation problems such as bleeding, efflorescence and solvent sensitivity[1] which are related to specific lipidic media and additives in the paint. Micro-analytical techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography/Mass spectrometry (GCMS) are routinely used for detection of organic materials in oil paints. The type of oil may be determined based on characteristic peak ratios of mainly palmitic and stearic acid, using GCMS. However, the techniques are less specific if other lipidic components are present. Moreover, using standard preparation techniques GCMS provides only limited information about important parameters which reflect the original composition and the state of ageing or degradation through oxidation, hydrolysis and soap formation. In general, a combination of analytical techniques and/or extensive sample pretreatment is required to obtain such information.[2,3]

This paper discusses 20th C oil paint technology and the organic components that may be present in fresh and dried oil paints.

An overview is given of novel mass spectrometric techniques which can be used for detection of these original materials and their drying and degradation products, and compared to GCMS techniques which involve pretreatment and derivatisation procedures.

Experimental

Characterization of paint samples was performed with direct MS methods: Evolved gas analysis (EGA)-MS,[4] (Direct Temperature-resolved MS (DTMS) and direct electrospray ionisation (ESI)-MS[2,5] as well as GCMS.[3] EGA-MS also involves 'heart-cut analysis' which involves cryo-trapping of desorbed fractions and subsequent GCMS analysis.[4] Typical sample sizes are 5-100 µg for EGA-MS, and c. 1-10 µg for ESI-MS.[5]

The analysed samples include 46 year old oil paint outs from Winsor&Newton, 2-4 year old homemade paints and microsamples from paintings by Karel Appel, Willem de Kooning and Jasper Johns.

Results

EGA-MS is a temperature-resolved mass spectrometric technique that allows for the fast separation and detection of free fatty acids, metal soaps (as additive or formed in the reaction of inorganic compounds with oil), the polymeric network as distinct fractions. Free fatty acids evaporate as such at lower temperatures, whereas metal soaps are recombined in the pyrolysis process to ketones and bound fatty acids are released as fragments of triglycerides. Ratios of palmitic and stearic acid in these fractions can then be used to give information of the type of drying oil(s) or added lipidic products such as metal stearates.

Degrees of oxidation and hydrolysis of very small samples in aged oil paints are studied with direct ESI-MS. This technique gives semi-quantitative information of fatty acids and glycerides and their degree of oxidation. The experiments clearly confirm the presence high oxidation and hydrolysis levels of the top layers of oil paints compared to underlying layers. In addition, the levels appear to relatively high for cured solvent sensitive paints.

Conclusions

EGA-MS and ESI-MS are useful and fast tools for providing data about the degradation products of the media and organic additives in oil paints. This information is shown to explain some of the problems associated with these paints, such as efflorescence and solvent sensitivity.

Acknowledgements

COLART, London, Old Holland, Driebergen, Talens, Apeldoorn. Jaap Boon / FOM institute AMOLF Amsterdam.

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