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# Recent Applications of Mass Spectrometry in Paint Analysis

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**Abstract**

Mass Spectrometry (MS) has wide applications in many fields, from biology and medicine and from chemistry and food industry. MS has also been successfully applied to the analysis of heavy metals, small molecules or large, polymeric molecules, and this analysis could be performed either by analyzing one molecule at the time or by analyzing simultaneously complex or very complex mixtures. Here we focus on several applications of MS in the analysis of paint, artist's paints, and powder coatings components reported recently in the literature.

## Introduction

Paint is a complex mixture of binder, or resins; coupled with pigments that impart the color; solvents; fillers; and various additives such as catalysts, UV stabilizers, flatteners, thickeners, that improve properties such as flow, foaming, skinning, finish, etc. Artists' paints are found either as oil-based paints, such as linseed oil, or water-based paints, including watercolor, acrylic paints, milk-paints, egg tempera, or wax-based paints. An additional type of coating are powder coatings, with a similar composition to paint, lacking the diluents or solvent; powder coatings are applied electrostatically and undergo a subsequent cure step at high temperature or under UV light.

Paint analysis has been performed historically for deformulation or reverse engineering, quality control, safety and regulatory compliance, defect analysis, forensics, or conservation and restoration in art and archeology. MS techniques have found wide use in paint analysis. MS has wide applications in many fields, from biology and medicine and from chemistry and food industry [1-4]. MS has also been successfully applied to the analysis of heavy metals, small molecules or large, polymeric molecules, and this analysis could be performed either by analyzing one molecule at a time or by analyzing simultaneously complex or very complex mixtures [2,5-11]. This review focuses on several applications of MS, specifically on Gas Chromatography-MS (GC-MS), Matrix Assisted Laser Desorption Ionization Time-of-Flight MS (MALDI-TOF-MS), Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and Liquid Chromatography-tandem MS (LC-MS/MS) in the analysis of paint, artist's paints, and powder coatings components, reported in the past five years.

## GC-MS

GC-MS was employed by Lluveras et al. [12] for the simultaneous quantification of glycerolipids, natural waxes, proteins, resin, and polysaccharides in only three extraction fractions from micro samples of paintings. Micro samples were exposed to a multi-step extraction technique: proteins and polysaccharides were ammonia-extracted, separated and purified on a $C_4$ sorbent, followed by hydrolysis; lipids and resins were saponifies/salified. The GC-MS method allowed quantitative analysis of aldoses and uronic acids, amino acids, mono-and dicarboxylic aliphatic acids, determining the presence of glycerolipids, animal and plant resins, proteinaceous and polysaccharide materials in paintings from Bamiyan Buddhas and a panel painting from the 15$^{th}$ century [12].

Drying oils in the 17$^{th}$ century painting La Encarnación in Granada, Spain, were easily identified by Manzano et al. [13] by GC-MS via eight fatty acid markers. Myristic acid (C(14:0)), palmitic acid (C(16:0)), stearic acid (C(18:0)), oleic acid (C(18:1)), linoleic acid (C(18:2)), suberic acid (2C(8)), azelaic acid, (2C(9)) and sebacic acid (2C(10)) were identified as markers for drying oils. The MS spectra of methyl ester derivatives of fatty acids following the derivatization with m-(trifluoromethyl)phenyl trimethylammonium hydroxide (TMTFAH) identified linseed oil, poppy seed oil and walnut oil in the La Encarnacion painting.

A pyrolysis GC-MS (Py-GC-MS) method was developed by Peris-Vicente et al. [14] for the analysis of commercial synthetic resins without sample pre-treatment. MS fragments with a structure resembling the monomeric unit were used as markers for resins. The method was successfully applied to a modern gluing material of a medieval reverse glass painting and to the binding medium of a painting by Georg Baselitz.

Py-GC/MS also allowed van der Werf et al. [15] to identify synthetic acrylic resins and Pinaceae resin, in a medieval crucifix panel painting in the Santa Maria a Mare church on the Isle of St. Nicholas (Isole Tremiti - Italy), painted on both sides, made between the late 12$^{th}$ century and the early 13$^{th}$ century and restored several times over the following centuries. The use of a complementary MS technique, MALDI-TOF-MS analysis, showed the occurrence of aged egg binder in a layer applied on animal glue and gypsum ground. These results confirmed the restorations, and determined that the painting was made by the 13$^{th}$ century Italian painting tradition.

## MALDI-TOF-MS

MALDI-TOF-MS is a complementary technique to GC-MS for analysis of paint samples. It is a highly sensitive technique, with a wide mass range, relatively unaffected by small amounts of salts and contaminants [7,16,17]. MALDI-TOF-MS was applied successfully in 2004 by Hynek et al. [18] for the identification of protein binders in paintings.

More recently, Triptovick et al. identified natural proteinaceous binders using MALDI-TOF-MS peptide mass finger printing coupled with tandem MS (MS/MS) experiments (TOF/TOF analysis) for more in depth identification of selected peptides, with minimal sample preparation prior to tryptic digestion. Peptide sequences from MALDI-TOF/TOF experiments determined the presence of animal glue and

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collagen in 19th century painting samples collected from Serbian church icons.

Hoogland and Boon [19] developed analytical methodologies by MALDI-TOF-MS, and Nanoelectrospray-Quadrupole-Time of Flight-tandem mass spectrometry (nano ESI–QTOF–MS/MS) with nozzle skimmer dissociation, to fully characterize poly (ethylene glycol) compounds in artists' acrylic emulsion paint products.

The molar mass distribution, the molar mass averages, the polydispersity index and the relative amount of a specific distribution for multiple PEGs were determined with MALDI-TOF, while nano-ESI-QTOF-MS enabled the end-group analysis [20]. Eight different manufacturer's paint media contained polyethylene glycol (PEG), polypropylene glycol (PPG) and a block copolymer of polyethylene glycol-polypropylene glycol (PEG-PPG) with molar mass averages ranging from 400 to 4200 Da, and nonylphenyl or an octylphenyl hydrophobic end-groups, or hydrophilic hydroxide and/or sulphate end-groups. The PEG composition of microsamples from a palette by David Hockney dating from 1970 and samples paintings by Patrick Caulfield (1936-2005) and John Hoyland (born in 1934) enabled to suggest which brand of paint was used by each artist [20].

Proteinaceous binders from animal glues, egg white and yolk, and milk casein, were easily distinguished by Fremout et al. [21] by MALDI-TOF coupled with multivariate analysis. Tryptic digests of egg temperas and animal glues were subjected to mass spectrometry followed by Principal Component Analysis (PCA) and Soft Independent Modeling of Class Analogy (SIMCA). Egg temperas and animal glues were analyzed, and glues were further separated in the multivariate analysis into different animal origins-mammal vs sturgeon. Paint samples from a 16th century altarpiece of St Margaret of Antioch in Slovakia were found to contain mammalian glue, despite degradation in time and small abundance in mass chromatograms.

In a more recent application, MALDI-TOF was used to analyze both proteins and lipids in paint layers. Van der Werf et al. [22] used an alternative denaturing agent, RapiGest™, in the Bligh-Dyer (BD) extraction, to extract both classes of compounds, and to improve digestion and purification of proteins. Triacylglycerols, phospholipids, their oxidation by-products, and proteins were identified in a late-15th century Italian panel painting pertaining to organic binders, such as egg, animal glue, casein, and drying oil. The influence of pigments on aging of lipids and proteins was also investigated [22].

Romero-Pastor et al. [23] examined the degradation process of proteinaceous binders due to the presence of historical mineral pigments, or Ultra Violet (UV) radiation, using MALDI-TOF and PCA. They were able to demonstrate in artificial models that the presence of pigments significantly influences the aging behavior of the binder.

## TOF-SIMS

In 2010, Mazel et al. [24] used cluster TOF-SIMS imaging to analyze uric acid and urate salts in rock art at the village of Songo in Mali. TOF-SIMS has been employed previously in organic analysis of cultural heritage paints [25]. Uric acid, snake urine, and a sample of a white pigment of a Dogon painting from the rock art site of Songo were compared in both positive and negative ion modes. TOF-SIMS analysis determined that the Dogon pigment contained uric acid, demonstrating for the first time that animal urine was used as a pigment by the Dogon [25].

Time-of-flight secondary ion mass spectrometry imaging using cluster primary ion beams was employed by Richardin et al. [26] for the identification of a green painting layer in the The Angels Concert scene from the 1516 Issenheim Altarpiece by Matthias Grünewald. TOF-SIMS was able to identify copper carboxylate clusters inside a basic copper chloride (atacamite) layer.

High resolution cluster-TOF-SIMS imaging allowed the characterization on a submicrometer scale of Rembrandt van Rijn's painting materials by Sanyova et al. [27]. The Portrait of Nicolaes van Bambeeck (1641) has been studied at a spatial resolution of 1 μm and 2 μm, revealing the presence of starch, proteins from shearings, and lead carboxylates from the reaction of lead white with the oils from the binding medium.

## LC-MS/MS

Liquid chromatography was also employed by Chambery et al. [28] in proteomic analysis by LC-ESI/QTOF MS/MS for the identification of protein binders in an early-twentieth-century mural painting from the St. Dimitar Cathedral in Vidin, Bulgaria. Egg and milk caseins were identified in the paint, alpha-casein proteolitic peptides serving as markers for different animal species for milk origin.

The hindered amine antioxidants and the degradation products of a polyester coil coating were investigated by Paine et al. [29] by liquid extraction surface analysis (LESA) coupled to a triple quadrupole (QQQ) QTRAP® 5500 MS, or LESA-MS/MS. TINUVIN®123 (bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate) and melamine, a degradation product of the thermoset polymer, were detected by the characteristic fragmentation pattern observed in LESA-MS/MS spectra. Powder-like deposits on the coatings surface (a defect known as "blooming") after long term exposure to outdoors were identified as melamine deposits.

Hindered amine light stabilizers; TINUVIN® 770, TINUVIN® 292, TINUVIN® 123 and TINUVIN® 152 were analyzed by Paine et al. [29] by yet another technique, paint spray MS. The technique involved the application of an external high voltage to a wetted sample of a thermoset polyester coil coating placed in front of the mass spectrometer inlet. The lack of requirement for sample pre-treatment makes the technique suitable as a rapid quality control technique.

Amines used as hardeners in epoxy resin systems, one tetramine, TETA (triethylenetetramine), and two diamines, IPDA (Isophorone diamine) and TCD-diamine (4,7-methano-1H-indene-5,?-dimethanamine, octahydro-), were analyzed by Dopico-Garcia et al. [30] in epoxy resin dust collected in workplaces. The amines were detected by HPLC with fluorescence detection. The derivatization of the amines with 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate was confirmed by MS on a hybrid linear ion trap LTQ Orbitrap mass spectrometer.

## Conclusion

In conclusion, over the past five years GC-MS, MALDI-TOF-MS and TOF-SIMS MS methodologies were employed for the elucidation of the composition of paints in art and archeology for conservation and restoration purposes. IN contrast, LC-MS/MS was employed for analysis of additives in both artists' paint for conservation purpose, and in modern coatings for quality control and environmental safety. Numerous complementary MS techniques are required to investigate the composition of paints due to the complex composition of the mixtures.

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