



Analysis of old master paintings by direct temperature-resolved time-of-flight mass spectrometry: Some recent developments[☆]



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ABSTRACT

Direct temperature-resolved mass spectrometry (DTMS) is an analytical technique in which small (μg) amounts of sample are applied to a filament and introduced into the ion source of a mass spectrometer. It is a fast fingerprinting method particularly suitable for the characterization of oils, resins, waxes, and other compound classes in tiny complex samples from paintings. DTMS results reported thus far have been obtained using instruments with nominal mass resolution. Higher mass resolutions can be achieved by magnetic sector mass spectrometers only at the expense of a severe loss of sensitivity. Modern time-of-flight mass spectrometers, however, do provide both high resolution and high sensitivity simultaneously. The availability of accurate mass information adds another dimension to DTMS. The difference between the nominal and accurate mass, the mass defect, may be graphically presented in so-called 'Kendrick plots'. These can be used as fingerprints, enabling a quick overview of the main features in high-resolution mass spectra of complex mixtures. This paper combines DTMS with Kendrick mass defect analysis applied to a series of reference compounds commonly found in paintings. Finally, we also present the results of analysis of samples taken from the 17th-century painting of *Saul and David* by Rembrandt van Rijn (Mauritshuis, The Hague) that has been recently subjected to extensive conservation treatment.

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1. Introduction

Direct temperature-resolved mass spectrometry (DTMS) is a fast fingerprinting method particularly suitable for the characterization of oils, resins, waxes, and other classes of organic compounds in tiny and complex samples of paintings (Fig. 1). It has been applied for the analysis of varnishes, organic pigments, and binding media [1–7]. Unlike gas chromatography mass spectrometry (GCMS), no pretreatment of the sample is required with DTMS. The sample is applied to a probe filament and directly introduced into the ion source of the mass spectrometer. The filament is heated by a programmed current, which results in volatilization of weakly bound and low molecular weight desorbing compounds at a low temperature, and pyrolysis of polymeric materials and inorganics at high temperatures. Typically, electron ionization is

applied as ionization technique with a low electron energy in order to reduce the formation of non-specific low mass fragment ions. Results are presented as total ion current (TIC) diagrams, from which mass chromatograms and summed mass spectra of selected events can be extracted. Principle component analysis (PCA) has been employed to cluster groups in large datasets [8–10]. DTMS has been used primarily for qualitative analysis. Quantitative analysis has proven difficult owing to matrix effects, particularly for complex paint samples containing multiple ingredients.

DTMS results reported thus far have been obtained almost exclusively by instruments with nominal mass resolution (whole numbers with no decimals). Although higher mass resolutions can be achieved by magnetic sector mass spectrometers, the sharp drop in sensitivity of such instruments with increasing mass resolution precludes their high-resolution operation in DTMS. Modern time-of-flight (TOF) mass spectrometers, however, provide high resolution and high sensitivity simultaneously. High-resolution mass spectrometry enables the distinction of nominally isobaric ions of different elemental compositions. The availability of accurate mass information (up to three decimals) adds another dimension to the data. The difference between the nominal and accurate mass, the mass defect, may be graphically presented in so-called 'Kendrick plots' (further explained in Section 3). Homologous

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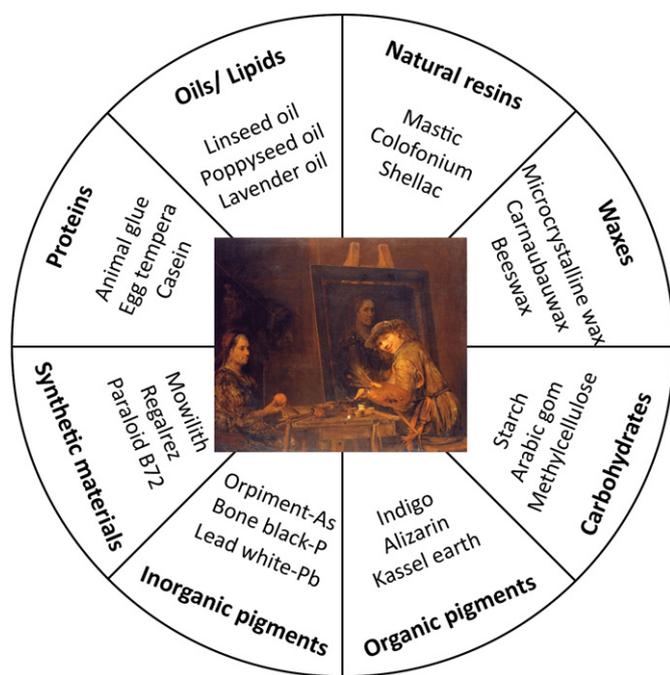


Fig. 1. Diagram showing the potential of DTMS to identify various classes of (in)organic compounds in microsamples of paintings.

series having a common repeating base unit will show in these plots as straight lines. The high duty cycle and consequently high sensitivity of time-of-flight instruments enables the use of smaller sample sizes and opens up new possibilities for combining DTMS with microscopic sample preparation techniques.

For this study, a series of compounds commonly found in paintings (see Section 2.1) were measured using a modern time-of-flight mass spectrometer to explore the advantages of the higher mass resolution and sensitivity for paint sample analysis, and to compile a reference atlas. The data were also graphically presented as Kendrick plots. Finally, we also present the results of analysis of samples taken from the 17th-century painting of *Saul and David* by Rembrandt van Rijn (Mauritshuis, The Hague). This painting has recently undergone extensive conservation treatment. During the treatment, blanching of an old surface coating occurred that required further analysis. DTMS was successful in the identification of this surface layer. This information was crucial for guiding the course of the conservation treatment. Here the Kendrick plots proved to be a handy tool for a visual comparison of the data. Some polymeric materials could be recognized as homologous ion series with its members lying on straight lines.

2. Materials and methods

2.1. Paintings and conservation reference materials

A list of the materials frequently encountered in historical paintings is given in Table 1. It includes natural resins and adhesives, synthetic conservation materials, gelling materials used in cleaning gels, and oil binding media.

2.2. Samples of the painting of *Saul and David*

During the treatment of the *Saul and David* painting, isolated sample material of the blanching surface coating was carefully collected with a scalpel and stereo-microscope for DT-TOFMS. Cotton swabs used for removal of the upper varnish layer and blanching layer were also analyzed. Table 2 lists the samples and sample locations. Further, samples were

Table 1

List of paintings and conservation reference materials measured with DT-TOFMS.

Description	Source
Dammar	Dry grains, MH
Mastic	Dry grains, MH
Shellac	Dry grains, MH
Colophony	Dry grains, MH
Paraloid B72	Dissolved in Shellsol A, MH
Laropal A81	Dissolved in Turpentine D, MH
Regalrez 1094	Dissolved in Turpentine D, MH
Rabbit skin glue	Dry grains, MH
Beeswax	Dissolved in turpentine, MH
Microcrystalline wax	Fresh, Renaissance
Cera alba	Dry grains, MH
Cera forlii	Dry grains, MH
Carbopol gel	Carbopol 954/ ethomeen C25/ acetone gel, MH
Carbopol 954	Powder, MH
Ethomeen C25	Liquid, MH
Pemulen TR2	Powder, MH
Linseed oil	Fresh, Talens
Linseed oil/vine black film	UvA-HIMS 2010
Linseed oil/ lead white film	UvA, C&R 2010
Lead ionomer	UvA-HIMS 2014 [16]
Lead palmitate	UvA-HIMS 2014 [16]
Lead azelate	UvA-HIMS 2014 [16]
Zinc ionomer	UvA-HIMS 2014 [16]
Zinc palmitate	UvA-HIMS 2014 [16]
Zinc azelate	UvA-HIMS 2014 [16]

MH—Mauritshuis Conservation Studio.

UvA-HIMS—University of Amsterdam, Van 't Hoff Institute for Molecular Sciences.

UvA-C&R—University of Amsterdam, Master Conservation& Restoration.

taken to prepare as paint cross-sections to localize the blanching in the paint layer build-up.

2.3. Direct temperature-resolved TOFMS

The mass spectrometer used was a Waters Micromass GCT Premier time-of-flight instrument with a mass resolution $M/\Delta M$ of 6000 at 200 Da and a mass accuracy typically within 20 mDa. DTMS was performed by means of a direct exposure probe equipped with a U-shaped Pt/Ir filament. The sample was applied onto the filament either as a small (1 μ l) droplet of a solution in toluene (reference materials) or a homogenized suspension in ethanol (paint samples) or, in the case of extremely small samples, as a single solid particle sucked into an ethanol droplet pre-attached to the filament under a microscope. The solvent was evaporated to dryness. During acquisition, the current through the filament was programmed from 0 to 1.8 A in 2 min. Electron ionization was applied with a low electron energy of 20 eV to enhance the relative abundance of molecular ions and structure-specific fragment ions. The ion source temperature was 180 °C. Data were acquired in a m/z range from 35 to 1050.

2.4. Cross-section preparation

The sample was embedded in Technovit 2000 LC mounting resin, a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer GmbH, Germany). The sample was polished to expose the complete paint layer build-up, with the assistance of a sample holder, on Micromesh sheets up to grade 12000 (Micro-Surface Finishing Products Inc., Wilton, Iowa, USA) [11].

2.5. Light microscopy

The embedded sample was first examined using a Leica DM2500 light microscope equipped with Leica DFC490 digital camera in the Mauritshuis. An Osram HBO 50 high-pressure mercury lamp and Leica filter A (excitation 340–380 nm, emission >425 nm) were used for UV-fluorescence microscopy.

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