Application Note No. 108 (March 2009)

Characterization of paint from artwork with automated THM pyrolysis and OPTIC Injector

Erwin Kaal, Geert Alkema

Introduction:

In the investigation of art-work, Pyrolysis GC-MS is extremely useful because solid samples can be direct introduced and a minimal of sample is required. However, pyrolysis of natural and polar materials results in polar fragments which are not accessible for GC. To overcome this limitation, THM-GC can be used; the polar (macro) molecules will be hydrolysed and methylated resulting in less polar fragments. The information obtained with THM-GC is very useful to find out which ingredients of paints, varnish, coatings and (natural) binders was used in artwork.
However, from a practical point of view, most conventional pyrolysis units like curry-point and filament pyrolysers are very limited in the possibility to perform THM-GC which as a consequence: not repeatable and qualitative results. With the OPTIC, this is now history, for solid samples as well soluble samples it is easy to get quantitative data. The whole THM-reaction is done inside the injector and therefore it is possible to control and optimize all the important parameters for performing repeatable THM-GC.
In this application note, THM-GC-MS is applied for the characterization of a complex sample which is representative for art-paint. The sample was prepared for a Round-Robin test which was organised by ICN (The Netherlands).

Sample material

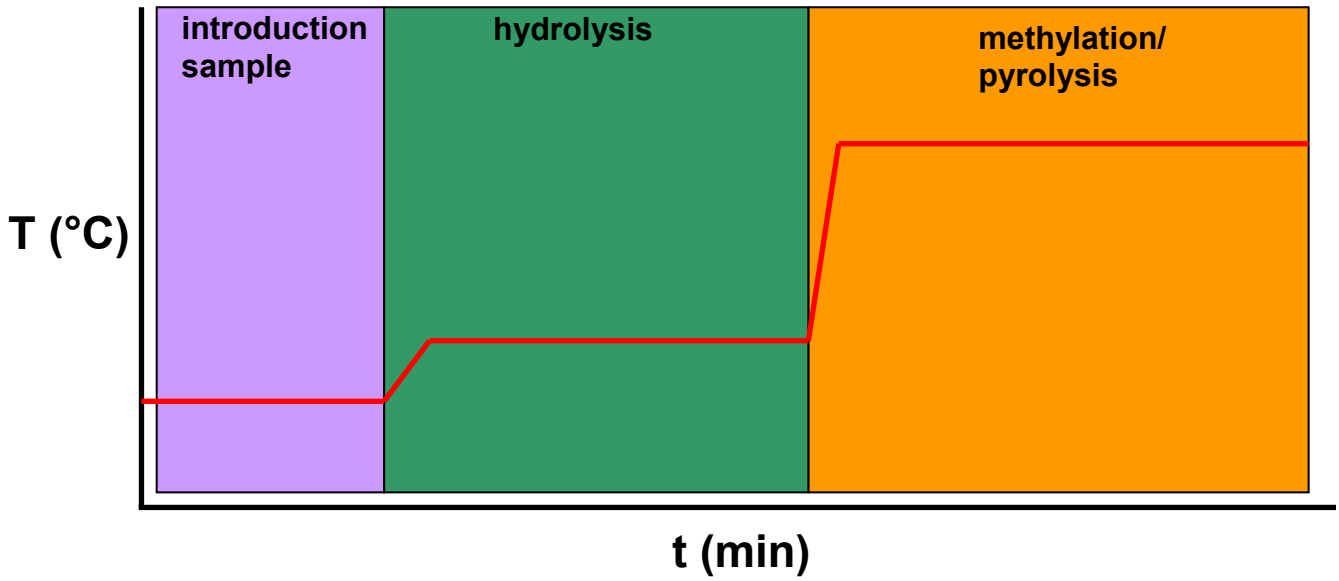
Dried Linseed oil with ultramarine Bleu
Paraloid B82 (EA/MMA resin)
Sandarac
Succinic acid
Mastic
Gum Arabic
Egg white (dry)

Experimental information about methods:

GC:

- Injector: OPTIC 3 Multi Mode Inlet in Pyrolysis mode
- Liner: Fritted liner + micro-cup
- Auto sampler: CombiPAL Robotic Sample Processor
- GC-MS: Shimadzu 2010
- GC-program: 40 °C (4 min); 7°C/min to 240°C; 10 °C/min 320 for 5 min
- GC column: TC-5 MS (30 m; 0.25mm ID and 0.25 µm film)

ATAS GL INTERNATIONAL B.V.
De Sleutel 9, NL-5652 AS Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79
E-mail: info@atasgl.com Internet: www.atasgl.com



THM parameters:

Introduction sample:	The sample was crushed into small fragments. These fragments were put into a microvail and 2 µl of tetramethylammoniumhydroxide (TMAH) in MeOH were added to the micro-vail and inserted into the fritted liner.
Introduction conditions:	Temperature: 40°C Split flow: 150 ml/min Column flow: 0.7 ml/min
Hydrolysis:	Temperature: 100 °C (ramp rate 10 °C/sec) for 120 sec.
Methylation / Pyrolysis:	Temperature: 550 °C (ramp rate 30 °C/sec) Split flow: 50 ml/min Column flow: 1.5 ml/min

ATAS GL INTERNATIONAL B.V.
De Sleutel 9, NL-5652 AS Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79
E-mail: info@atasgl.com Internet: www.atasgl.com

Results:

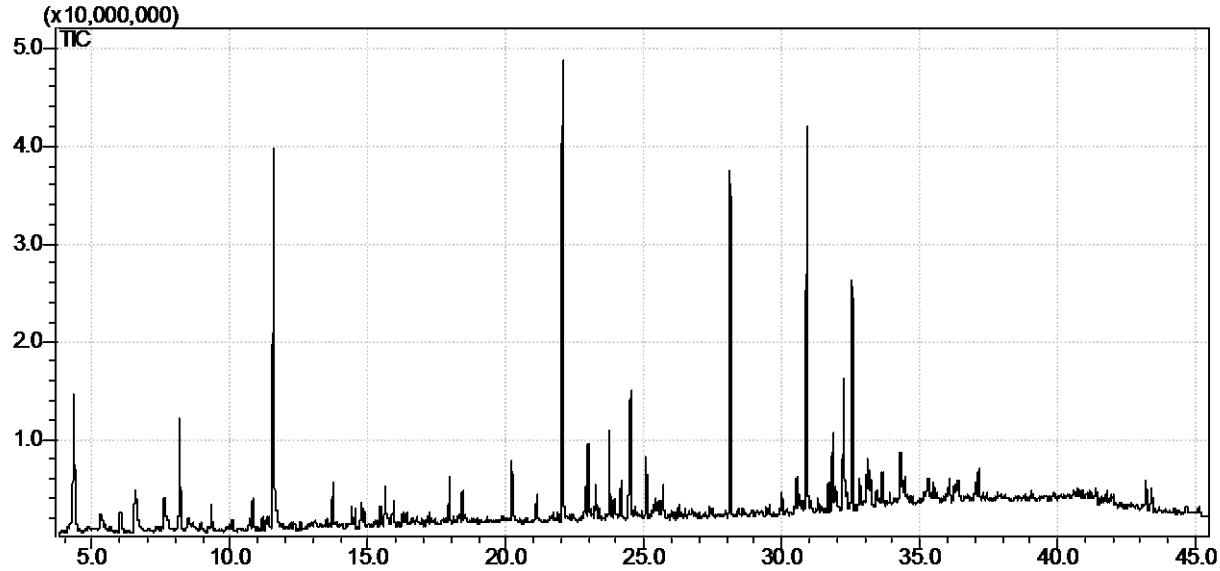


Figure 1: TIC-chromatogram of THM-GC of the Round-Robin sample.

Discussion:

All ingredients of this complex oil-wax-resin sample were identified. For example, the acrylic resin (paraloid B82) was confirmed by the presence of MMA and EA. Linseed oil was identified by the presence of glycerol and several fatty acids and fatty di-acids (Figure 2). The di-methylester coming from succinic acid is present (marker for Amber). For the identification of Sandarac the presence of a hydroxyl form of sandaracopimaric acid (Figure 3). In the last part of the chromatogram, derivatives of the mastic and some other triterpenoid were detected.
This sample was finally 10 times analysed with the injector THM-procedure. For the calculation of the RSDs, peak areas of 10 identified compounds were used. For those compounds the RSD was ranging from 2.1% to 8.9%.

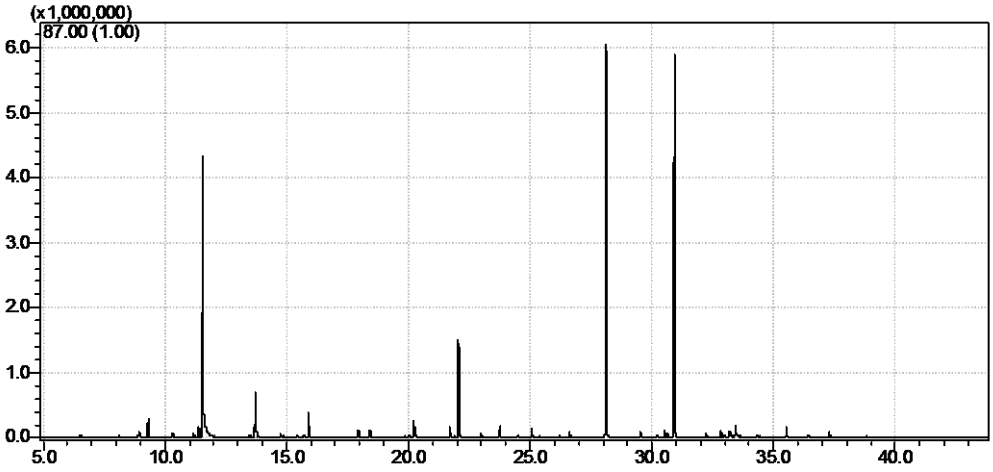


Figure 3: Selected ion m/z 87 to show all the methylated fatty acids.

ATAS GL INTERNATIONAL B.V.
De Sleutel 9, NL-5652 AS Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79
E-mail: info@atasgl.com Internet: www.atasgl.com

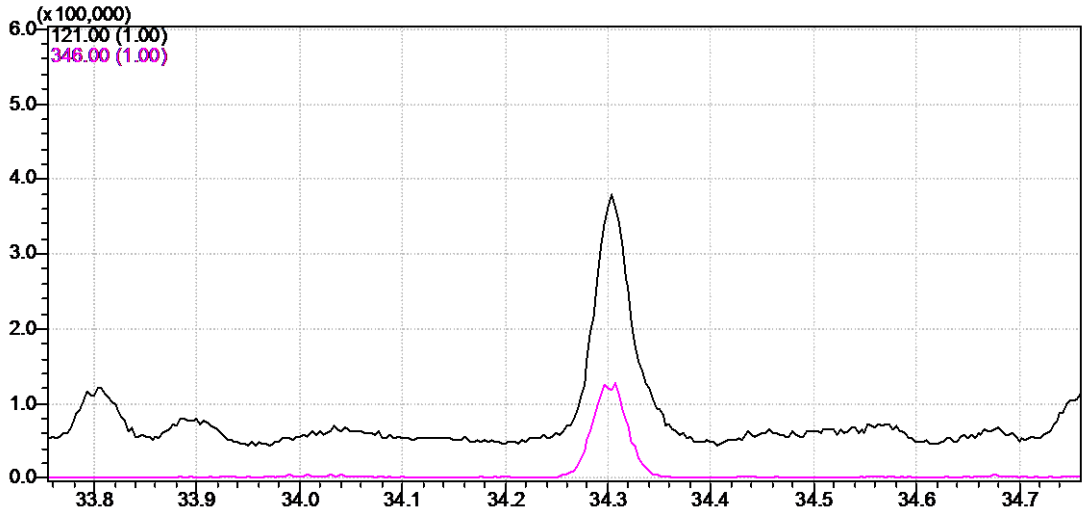


Figure 3: Selected ions m/z 121 (blanc) and m/z 346 (pink) of hydroxyl form of sandaracopimaric acid .

Conclusion:

THM-GC of complex samples can be done inside the OPTIC injector. Quantitative results can be obtained using this novel method. The whole method is fast and reliable.

ATAS GL INTERNATIONAL B.V.
De Sleutel 9, NL-5652 AS Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79
E-mail: info@atasgl.com Internet: www.atasgl.com