SHIMADZU

Application Data Sheet

No.36

GCMS

Gas Chromatograph Mass Spectrometer

Characterization of Paint from Art Work Using Automatic Reactive Pyrolysis in the OPTIC-4 Inlet

Pyrolysis GC-MS provides an extremely useful method for art research, because it allows solid samples to be directly analyzed and requires only small sample quantities. However, pyrolysis of natural polar substances can generate polar compounds that cannot be measured by GC. To overcome this limitation, the thermally assisted hydrolysis and methylation-gas chromatography (THM-GC) method can be used. This method converts polar macromolecules into weakly polar hydrolyzed and methylated degradation compounds. The information obtained from THM-GC is useful for identifying the composition of paints, varnishes, coatings, or binders (natural) in art work.
However, performing THM-GC methods using a Curie-point or filament type pyrolyzer can result in problems with repeatability or quantitative analysis. In contract, the OPTIC-4 enables performing all THM reactions within the inlet. Therefore, by optimizing the TMH conditions, it enables obtaining good repeatability.
This datasheet presents the results from applying the THM-GC/MS method to characterize complicated samples characteristic to paint from air work.

Experiment

Sample

Ultramarine blue linseed oil, PARALOID™ B-82 (a Dow brand name for a synthetic EA/MMA resin), sandarac (plant resin), succinic acid, mastic (plant resin), gum arabic (plant resin), and egg white (dried)

Sample Preparation

Samples are crushed into fragments. Fragments are placed in micro vials, then 2 µL of a tetramethylammonium hydroxide (TMAH) methanol solution is added to the micro vials. These are inserted in the fritted liner.

Table 1: Analysis Conditions

Instruments

Inlet:	OPTIC-4 injector Multi Mode Inlet in Pyrolysis mode (ATAS GL International BV)
Liner:	Fritted liner + Micro-vial (ATAS GL International BV)
GC-MS:	GCMS-QP2010 Ultra (Shimadzu Co.)
Autosampler:	AOC-5000 Plus (Shimadzu Co.)
Column:	TC-5 MS (30m x 0.25 mm I.D., df=0.25 µm (GL Science)

Injection Parameters

THM Parameter （Figure 1）

Inject Condition

Temperature : 40℃

Split flow rate : 150 ml/min

Column flow rate: 0.7 ml/min

Hydrolyze :

Temperature: 40 ℃ → (10℃/ min) → 100℃(120sec)

Methylation/ Thermal decomposition :

Temperature : 100 ℃ → (30℃/ min) → 550℃

Split flow rate : 50 ml/min

Column flow rate: 1.5 ml/min

GC

Column oven temperature:

40℃(4min) → (7℃/ min) → 240℃ →(10℃/ min) → 320℃(5min)

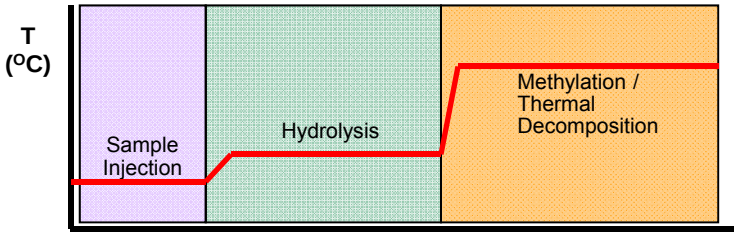

Fig. 1: THM Temperature Profile

MS

Interface temperature : 280℃

Ion source temperature: 250℃

Solvent elution time : 3.5min

Data sampling time : 3.5 – 45.5min

Measurement mode : Scan

Mass range : *m/z* 40-500

Results and Discussion

Standard Sample Measurement

A total ion current chromatogram of a round robin test sample measured by THM-GC-MS is shown in Figure 2.

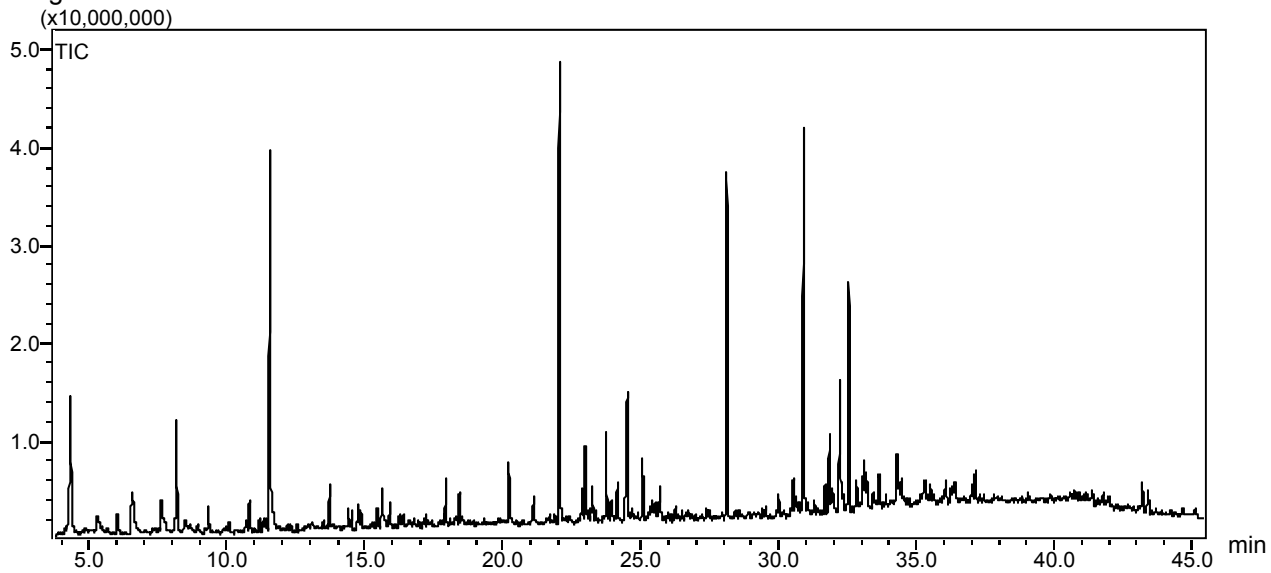

Fig. 2: Total Ion Current Chromatogram of Round Robin Test Sample Measured by THM-GC-MS

The complicated compositions of all oils, waxes, and resins in the sample were identified. For example, the presence of acrylic resin (PARALOID™ B-82) was confirmed by the presence of MMA and EA. Linseed oil was confirmed by the presence of glycerol, multiple monocarbonic acids and dicarbonic acids (Fig. 3). Dimethyl esters from succinic acid were detected (markers for the plant resin amber). Sandarac was confirmed as a hydroxide of sandaracopimaric acid (Fig. 4). In the second half of the chromatogram, mastic and several other derivatives of triterpenoid were detected.
This sample was analyzed using the THM inlet procedure 10 consecutive times. %RSD values calculated based on the peak areas for the 10 compounds identified ranged from 2.1 % to 8.9 %.

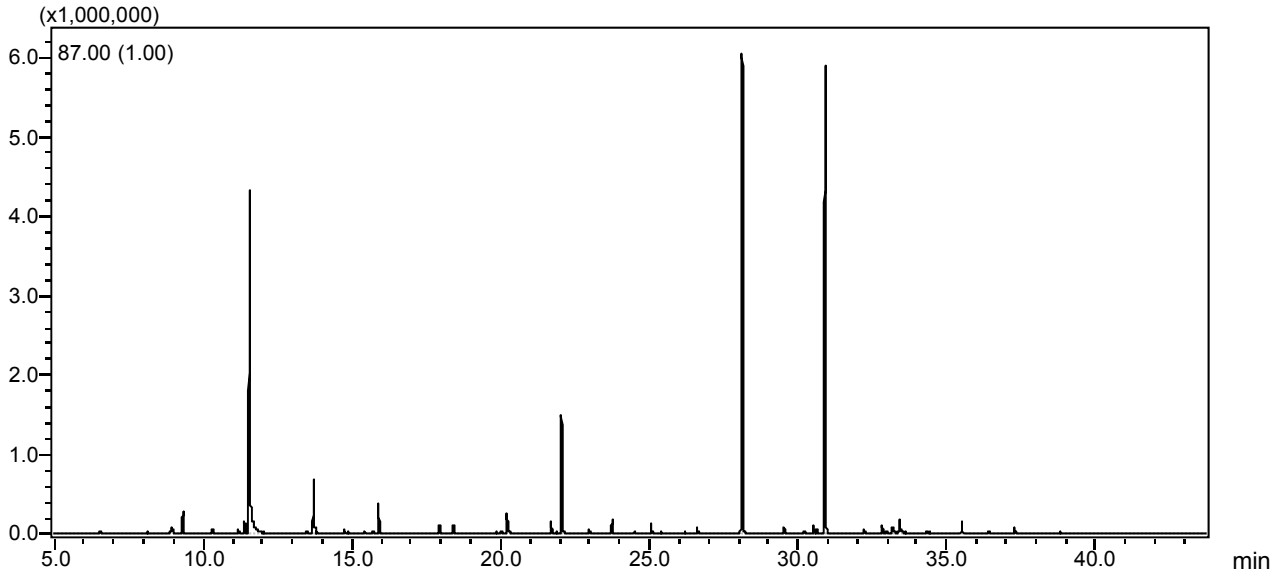

Fig. 3: Mass Chromatogram of Ions Characteristic to Fatty Acid Methyl Esters at *m/z* 87

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