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Technical Report

Utility of a System Consisting of EGA/PY-3030D and GCMS-QP2010 Ultra

– Analysis of Eyeliner and Pyrolysis of a Mural Paint at 1000°C –

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Abstract:

The analysis of eyeliner and museum quality paint are used to demonstrate the capabilities of a system consisting of an EGA/PY-3030D pyrolyzer and a GCMS-QP2010 Ultra. The eyeliner was first analyzed using evolved gas analysis (EGA-MS). The EGA thermogram shows that the eyeliner contains compounds with a wide range of properties – from volatile organic solvents to nonvolatile polymers. The compositional analysis of each temperature zone on the EGA thermogram was determined using a high-resolution capillary column interfaced to the GC-MS. The high temperature pyrolysis of an ancient mural paint illustrates of the value of pyrolysis-GC-MS to characterize a material of interest.

Keywords: Py-GC/MS, TG-MS, pyrolyzer, EGA, Heart-Cut EGA-GC-MS, cosmetic, mural paint

1. Introduction

Pyrolysis (Py)-GC/MS of polymeric materials in all forms can routinely be performed with no sample pre-treatment and often provides unique information about the composition of the sample. This makes it an extremely useful tool for polymer characterization.[1–5] However, normal flash pyrolysis (single-shot) of a sample generates a pyrogram that contains not only the pyrolyzates of the polymer but also "peaks" for all other compounds present. This often makes it difficult to determine the origin of each peak in the pyrogram.

Evolved gas analysis (EGA)-MS utilizes the ability to precisely program the temperature of the sample in the micro-furnace from a low to a high temperature. The resulting EGA thermogram provides the analyst with a highly reproducible indication of the sample complexity.[2, 6, 7] Also this system can be configured to perform heart-cut EGA-GC/MS analysis. That is, each temperature zone in the EGA thermogram is automatically introduced into a separation column for GC-MS analysis.[8–10]

In this report, eyeliner is used as an example of a complex material containing a wide boiling point range of constituents: volatiles up to polymeric components. The analysis of each EGA thermal zone facilitates the complete characterization of the organic constituents in the sample.

Using the temperature programming function and high temperature capability of the EGA/PY-3030D, the composition of an ancient mural paint can easily be determined.

2. Experimental

Sample collection

A commercial eyeliner (TT Tony Tanaka, max hold eyebrow, brown EB02) was used as an example of a complex material containing multiple volatiles and polymers. Fig. 1 shows how the tip of the eyeliner was used to coat a thin film (*ca*. 0.5 mg) on the inner wall of a sample cup. The sample was analyzed using the analytical conditions described in Table 1.

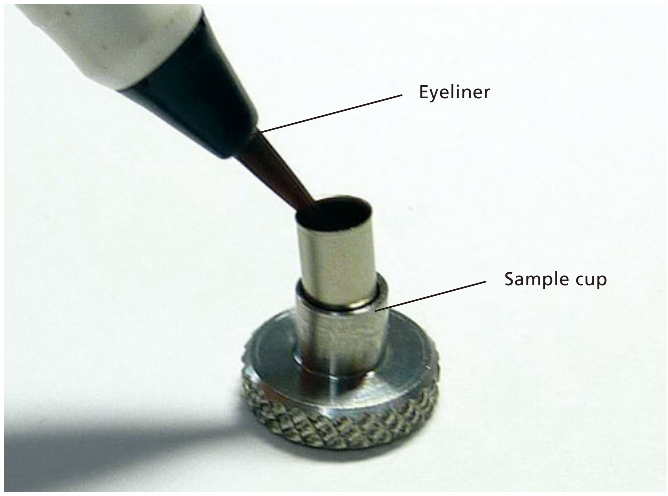

Fig. 1 Collecting eyeliner sample in an Eco cup.

1 Frontier Laboratories Ltd.

3. Instrument

The analytical system consisted of a micro-furnace based Multi-Shot pyrolyzer (EGA/PY-3030D, Frontier Laboratories Ltd.) and a GCMS-QP2010 Ultra, Shimadzu Corp. The system configuration is shown in Fig. 2. The pyrolyzer is directly interfaced to the split/splitless injector of the GC. When doing an EGA analysis, the injector is directly connected to the MS through a deactivated EGA tube (no stationary liquid phase, L=2.5 m, id=0.15 mm). The GC oven temperature is isothermal at 250°C, and gases evolved from the sample (as it is heated from 40°C to 600°C (or up to 1050°C) at 20°C/min) were immediately introduced into the MS without separation. Therefore, the evolved gases can be monitored in real time.

If the EGA tube is connected to the MS using a Vent-Free GC/MS adaptor[11] (Frontier Laboratories Ltd.), switching from an EGA tube to a separation column takes just a few minutes. This is done without venting the MS.

Heart-cut EGA-GC/MS analysis uses the Selective Sampler (SS-1010E, Frontier Laboratories Ltd.) to either selectively "vent" compounds that are not of interest or introduce gases of interest to a separation column. During the heart-cutting, the sample vapors must be "held" at the head of the column. This can often be accomplished by using a low Initial temperature. If the evolving vapors can not be held using column temperature, a MicroJet Cryo-Trap (MJT-1030Ex) can be used to cryo-trap low boiling gases at the head of the separation column. The trapped gases are later thermally desorbed prior to GC/MS analysis.

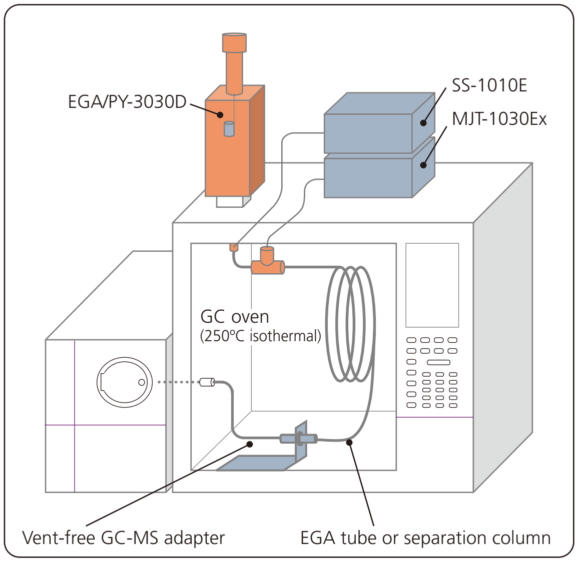

Fig. 2 System configuration for EGA-MS and heart-cut EGA-MS

Table 1 Analytical conditions

	EGA-MS	Heart-cut EGA-GC-MS
Instruments		
Pyrolyzer	: Multi-Shot Pyrolyzer 3030D (Frontier-Lab)	Multi-Shot Pyrolyzer 3030D (Frontier-Lab)
GC-MS	: GCMS-QP2010 Ultra	GCMS-QP2010 Ultra
Column	: EGA Tube 2.5 × 0.15 mm I.D. (Frontier-Lab)	Ultra ALLOY-5 (MS/HT) (L: 30 m, ID: 0.25 mm, df: 0.25 μm Frontier-Lab)
Analytical Conditions		
Pyrolyzer		
Furnace Temp	: 40°C (0 min) - (20°C/min) - 600 or 1000°C (0 min)	40°C (0 min) - (20°C/min) - 600 or 1000°C (0 min)
Py-GC ITF Temp.	: Max 320°C (Auto Mode)	Max 320°C (Auto Mode)
GC		
Injection Temp.	: 300°C	300°C
Column Temp.	: 250°C (isothermal)	40°C (0 min) - (20°C/min) - 320°C (0 min)
Injection Mode	: Split	Split
Carrier Gas	: He (constant linear velocity mode：124.2 cm/sec)	He (constant linear velocity mode：31 cm/sec)
Split Ratio	: 1/50	1/50
Sample amount	: *ca.* 0.5 mg	*ca.* 0.5 mg
MS		
Ion Source Temp.	: 250°C	250°C
Interface Temp.	: 280°C	280°C
Scan Range	: *m/z* 29 - 600	*m/z* 29–600
Event Time	: 5 sec	0.3 sec
Scan Speed	: 116 amu/sec	2,000 amu/sec

4. Results

Results obtained by EGA-MS

The EGA-MS thermogram of the eyeliner is shown in Fig. 3a. Zones A through C contain solvents and additives, while zones D and E contain polymers. These results show that the eyeliner contains a wide variety of compounds ranging from low boiling to high boiling compounds.

Identification of volatiles by GCMSsolution

In EGA-MS, a normal separation capillary column is not used; therefore, a peak often represents multiple compounds This is clearly shown in the two-dimensional multi-ion chromatogram using the two dimensional display feature of F-Search (Fig. 3b). For example, peaks observed in zone A seem to be essentially the same in peak shape and apex temperature. In this case, as illustrated in Fig. 4, the main component in zone A is identified as 1,3-butanediol by the NIST library search capability found in GCMSsolution.

On the other hand, in zone B, multiple volatile compounds are easily observed. In a case like this, identification cannot be done using the EGA alone, Each zone must be analyzed independently using heart-cut EGA-GC/MS.

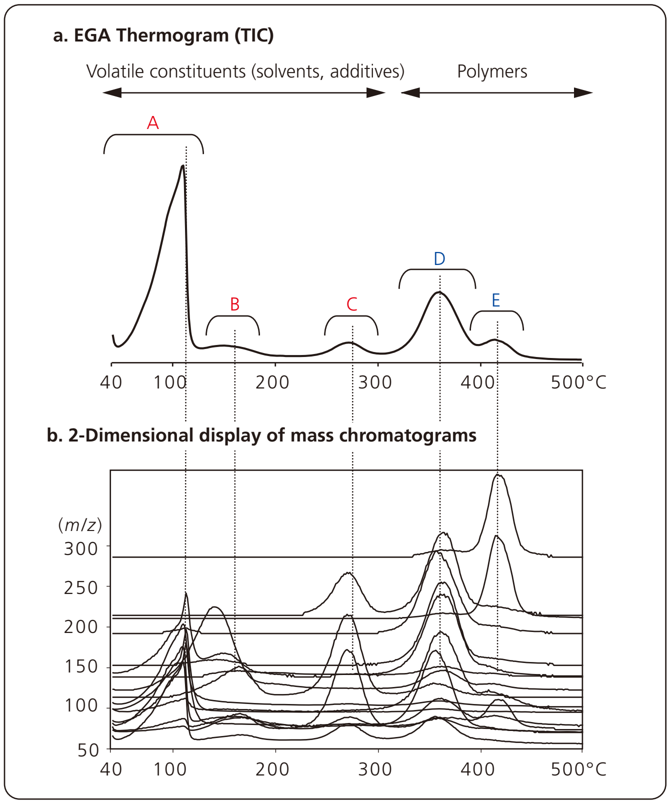

Fig. 3 EGA thermogram of eyeliner and analysis using mass chromatograms

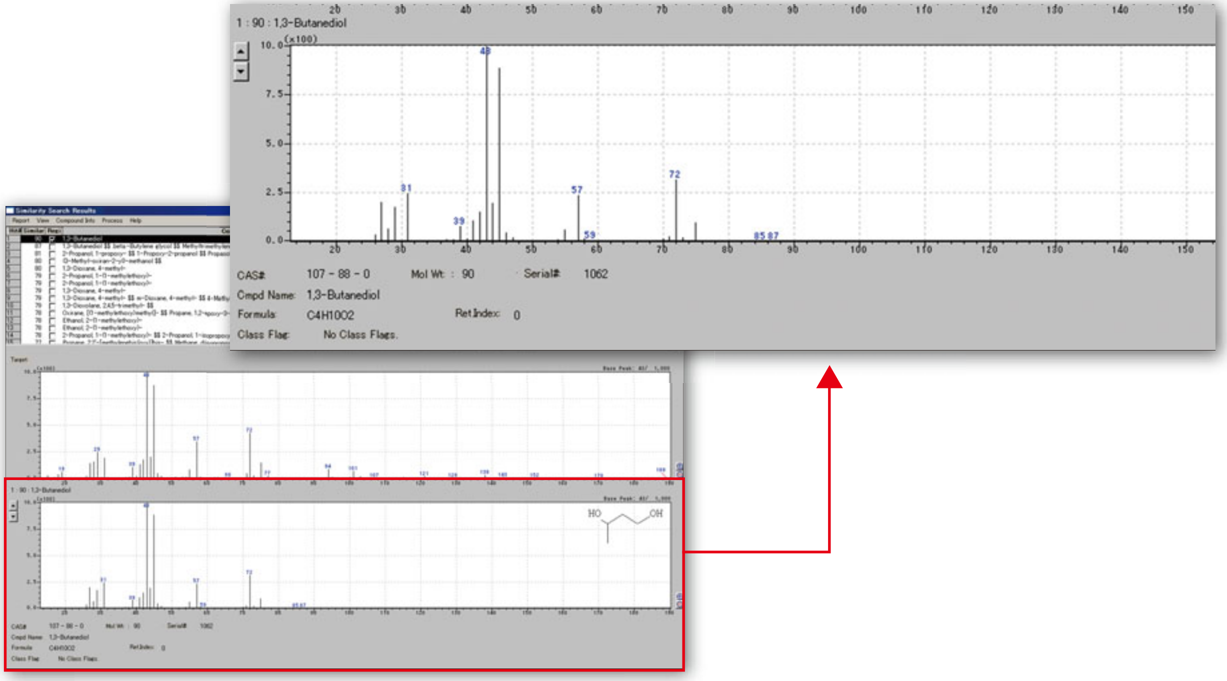

Fig. 4 Search results for peak A obtained using NIST library of GCMSsolution

Results of heart-cut EGA-GC/MS

The heart-cut GC/MS results of the zones A through E observed on the EGA thermogram (Fig. 3) are shown in Fig. 5. Zone A contains 1,3-butanediol as well as a number of other volatiles, while in zones B and C, relatively high boiling compounds derived from additives are observed. On the other hand, methyl methacrylate (MMA) as a pyrolyzate of the polymer observed in zone D. This is the monomer of poly-methylmethacrylate (PMMA), which is a polymer commonly used for paints, and is formed by the pyrolysis of PMMA.[1)] In zone E, a series of cyclic dimethylsiloxanes derived from pyrolysis of poly-dimethylsiloxane are observed.[1)]

As described above, detailed analysis can be accomplished by sequentially heart-cutting each of temperature zones in the EGA thermogram (Fig. 3) and introducing them into a separation column for GC/MS analysis.

Compositional analysis of an ancient mural painting unearthed from ruin

Because the upper limit temperature of the multi-shot pyrolyzer micro-furnace is 1,050°C, not only organic compounds but a variety of inorganic compounds can be analyzed. The compositional analysis of an ancient mural painting (photo shown in Fig. 6) is described as an example.

An EGA thermogram of the brown section of the mural shown in Fig. 6 is given in Fig. 7.

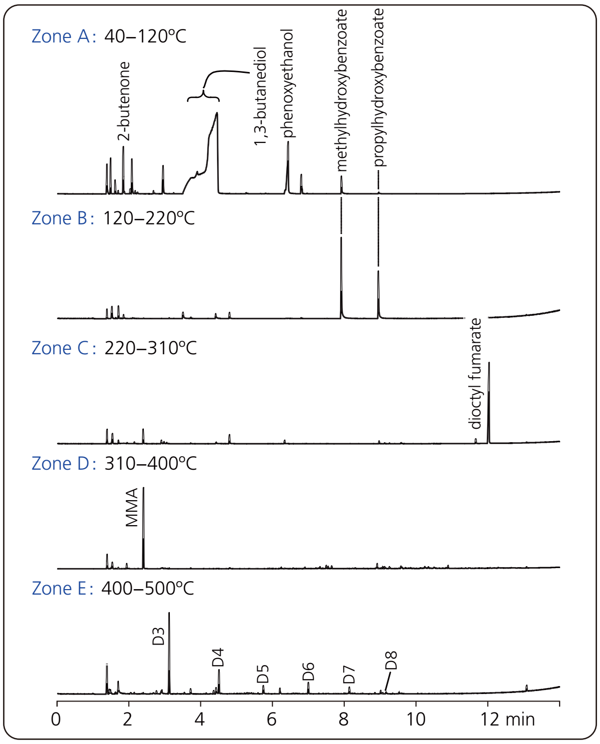

Fig. 5 Heart-cut EGA-GC/MS analysis of zones A to E of EGA thermogram of an eyeliner

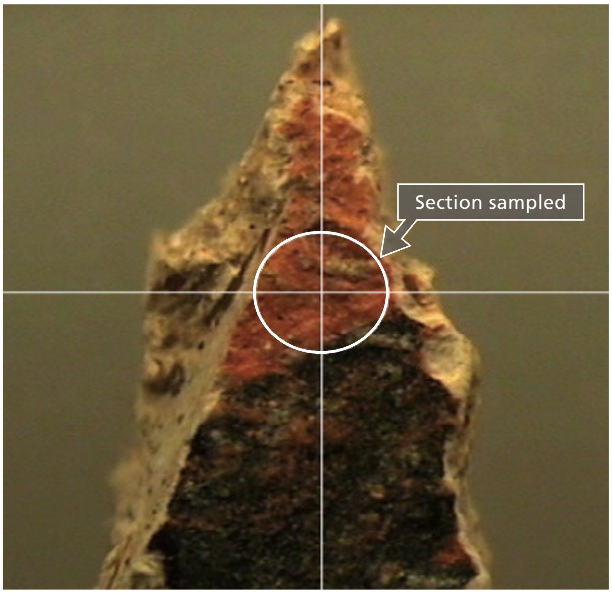

Fig. 6 A small fragment of ancient mural unearthed from ruins

Saturated hydrocarbons originated from natural wax were observed in the mural paint constituents in the temperature zone up to 600°C. In the range of 600 to 800°C, CO_2 was observed, and from 850 to 1000°C a cyclic sulfur compound was observed. These are derived from the carbonates and sulfates of calcium and iron as determined by the EDX elemental analysis using SEM.

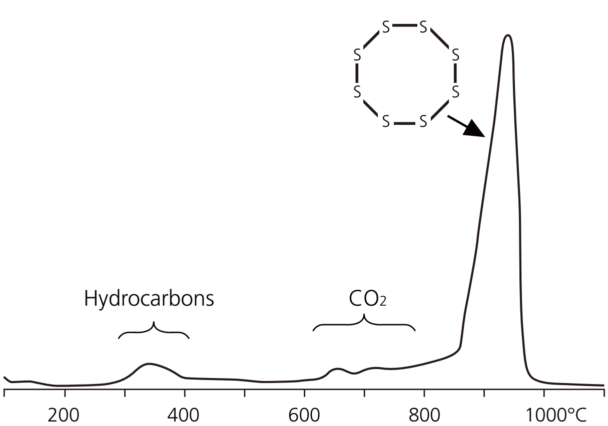

Fig. 7 EGA thermogram (TIC) of ancient mural

5. Conclusion

Samples of eyeliner and mural paint were analyzed using a EGA/PY-3030D pyrolyzer interfaced to a GCMS-QP2010 Ultra EGA-MS and heart-cut EGA-GC/MS methods, used in this study, provided a nearly complete characterization of the two demonstration samples. The study indicates that the multi-shot pyrolyzer EGA/PY-3030D can be used to characterize a wide variety of complex materials ranging from volatile organics, to polymers, and even some inorganic materials. These techniques can be applied to many application needs in the cosmetics, paints, coatings, dyes, pigments and museum conservatory market sectors.

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