TECHNICAL NOTE

Thermal Analysis

Analysis of an Unknown Aqueous Sample by TG-IR-GC/MS

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Introduction

A laboratory often must analyze an unknown mixture to determine the primary components and identify additives or contaminants. This information may be needed, for example, to evaluate a competitor's product or to determine compliance with regulations. The use of spectroscopic techniques to identify isolated molecular components is well established, and the separation and isolation can be accomplished by thermogravimetric analysis (TGA), FT-IR, and gas chromatography (GC). However, often combining these techniques is more powerful approach for complex mixture. PerkinElmer makes a range of hyphenated solutions and in this case, the TL-9000 transfer line is used to allow TG-IR-GCMS analysis on one sample. The laboratory apparatus combining these techniques can be seen in Figure 1.

Figure 1. From left to right: PerkinElmer® Clarus® 6000 GC/MS, PerkinElmer® Frontier® FT-IR, The Pyris® 1 TGA and the TL9000 temperature control module. The black transfer lines are part of the TL9000 interface system.

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For the Better

Consider the recent example: An analytical lab has received a pigmented aqueous sample for analysis.

Since water interferes strongly with the analysis, the sample was first dried at ambient temperatures. When the drying process was complete the film thus obtained was detached from the drying tray and warmed briefly in a dry air flow. A sample was then taken from the resultant film and placed in a TGA coupled to an infrared spectrophotometer (TG-IR). The twenty milligram sample was heated from 20 to 850 °C at a rate of 20 °C/min in a nitrogen atmosphere. During the heating of the sample, the gas released by the sample was directed to the gas cell of an infrared spectrophotometer via the TL8000 heated transfer line and interface. So during the TGA analysis, spectra of the gas released by the sample during heating were analyzed iteratively. See Figure 2 for the thermal weight loss versus temperature curve.

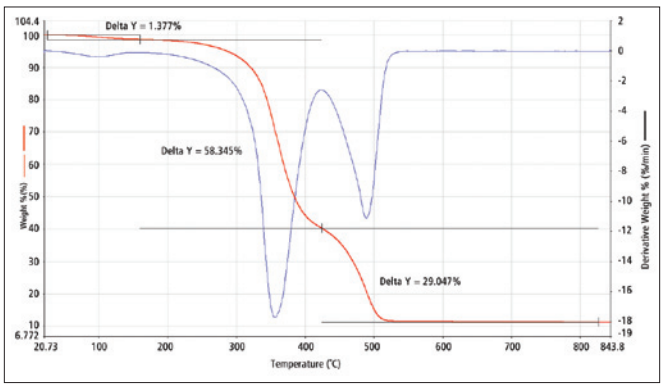


Figure 2. Weight loss (red curve) and rate of weight loss (blue curve) versus temperature from ambient to 850 °C.

Between 20 and 150 °C there was a weight loss of 1.38% from residual moisture in the sample. Between 200 and 410 °C there was a significant weight loss from evaporation of volatile fractions, accompanied by an initial decomposition of the polymer. The final decomposition of the polymer occurred between 410 and 510 °C.

During the TGA thermal separation, the gases released by the sample were sent to the FT-IR for spectral analysis. The TG-IR data consists of a sequence of spectra, acquired at intervals of around 8 seconds. The standard presentation of the data is the adsorption versus wave number, and this spectral profile of the gases released by the sample is generated for each roughly two degree interval. The TG-IR Spectrum Time Base software provides a 3D graphical representation, consisting of stacked IR spectra, a feature that provides a snapshot of the entire TG-IR separation (see Figure 3). This aids in interpreting the kinetics of the decomposition process and deciding which temperature cuts to analyze. Furthermore, the analyst can view the absorption versus time at any chosen wavelength to track the relative concentration of a particular decomposition product versus time, hence, temperature.

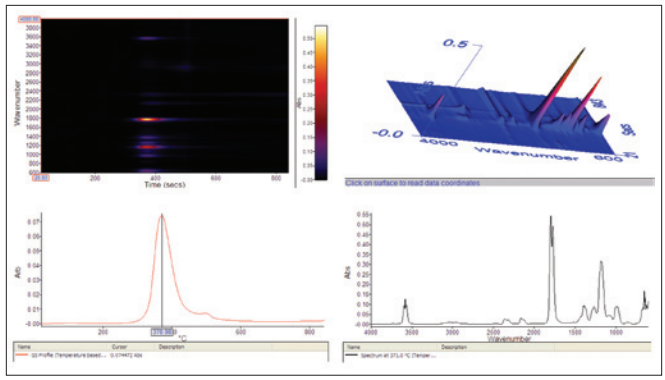


Figure 3. Spectrum Time-Based software outputs, which aid in interpreting the decomposition process. With experience, an operator will look at the stacked spectra (upper right plot) and see an "unexpected mountain range" that represents the transient presence of a particular species of off-gassing product of potential interest.

With reference to the data in Figure 3 the author observed the evaporation of an unknown substance which reached a concentration maximum at about 280 °C. The spectrum at this temperature was selected for a database search. From this library search the unknown substance was found to be triethylene glycol dibenzoate – or a very similar substance. Figure 4 shows that spectra of the unknown and that of the best search match. Figure 5 lists other match candidates together with the relative statistical likelihood of each match.

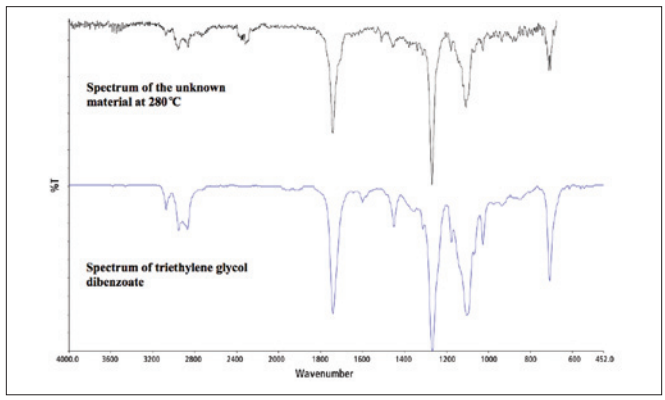
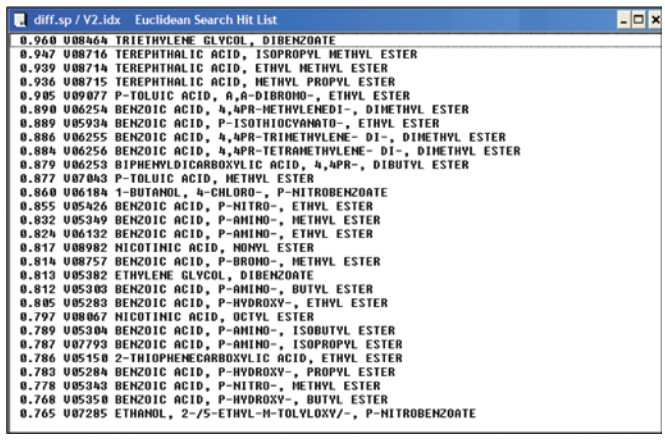


Figure 4. Best match spectra using PerkinElmer Spectrum Search software.


diff.sp / V2.idx Euclidean Search Hit List

0.960	V08464	TRIETHYLENE GLYCOL, DIBENZOATE
0.947	V08716	TEREPHTHALIC ACID, ISOPROPYL METHYL ESTER
0.939	V08714	TEREPHTHALIC ACID, ETHYL METHYL ESTER
0.936	V08715	TEREPHTHALIC ACID, METHYL PROPYL ESTER
0.905	V09077	P-TOLUIC ACID, A,A-DIBROMO-, ETHYL ESTER
0.890	V06254	BENZOIC ACID, 4,4PR-METHYLENEDI-, DIMETHYL ESTER
0.889	V05934	BENZOIC ACID, P-ISOTHIOCYANATO-, ETHYL ESTER
0.886	V06255	BENZOIC ACID, 4,4PR-TRIMETHYLENE- DI-, DIMETHYL ESTER
0.884	V06256	BENZOIC ACID, 4,4PR-TETRAMETHYLENE- DI-, DIMETHYL ESTER
0.879	V06253	BIPHENYLDICARBOXYLIC ACID, 4,4PR-, DIBUTYL ESTER
0.877	V07043	P-TOLUIC ACID, METHYL ESTER
0.860	V06184	1-BUTANOL, 4-CHLORO-, P-NITROBENZOATE
0.855	V05426	BENZOIC ACID, P-NITRO-, ETHYL ESTER
0.832	V05349	BENZOIC ACID, P-AMINO-, METHYL ESTER
0.824	V06132	BENZOIC ACID, P-AMINO-, ETHYL ESTER
0.817	V08982	NICOTINIC ACID, NONYL ESTER
0.814	V08757	BENZOIC ACID, P-BROMO-, METHYL ESTER
0.813	V05382	ETHYLENE GLYCOL, DIBENZOATE
0.812	V05303	BENZOIC ACID, P-AMINO-, BUTYL ESTER
0.805	V05283	BENZOIC ACID, P-HYDROXY-, ETHYL ESTER
0.797	V08067	NICOTINIC ACID, OCTYL ESTER
0.789	V05304	BENZOIC ACID, P-AMINO-, ISOBUTYL ESTER
0.787	V07793	BENZOIC ACID, P-AMINO-, ISOPROPYL ESTER
0.786	V05150	2-THIOPHENECARBOXYLIC ACID, ETHYL ESTER
0.783	V05284	BENZOIC ACID, P-HYDROXY-, PROPYL ESTER
0.778	V05343	BENZOIC ACID, P-NITRO-, METHYL ESTER
0.768	V05350	BENZOIC ACID, P-HYDROXY-, BUTYL ESTER
0.765	V07285	ETHANOL, 2-/5-ETHYL-M-TOLYLOXY/-, P-NITROBENZOATE

Figure 5. Output of Search software, showing match candidates.

Next, the TL9000 interface was enlisted to perform a subsequent analysis to confirm the identity of the unknown substance in the sample. At the time of maximum concentration absorbance of the substance being analyzed, the gas in the IR gas cell was sent to a GC/MS. The gas chromatogram can be seen in Figure 6.

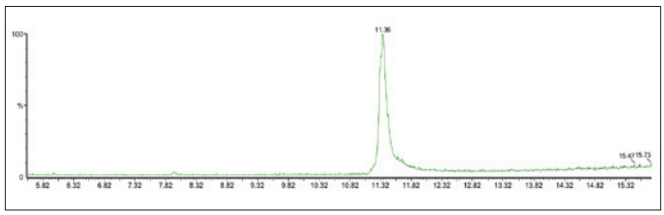


Figure 6. GC Chromatogram, detection amplitude versus time in minutes.

The material which came off the TGA at 280 °C, and which was further resolved by GC, was then evaluated by mass spectrometry (MS), whereby the unknown molecular structure is broken up into constituent ions that are then identified by their flight response in a magnetic field. The results are compared to a library of established MS data.

The National Institute of Science and Technology (NIST®) MS database search for the unknown substance yielded the output in Figure 7.

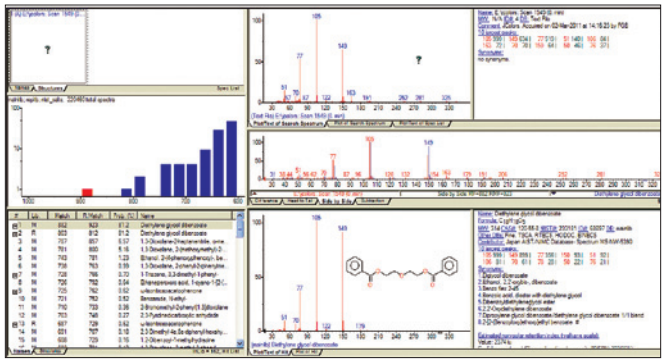


Figure 7. Output of TurboMass™ software showing the MS spectral results and the results of the search of the NIST® MS database.

The unknown substance was found to be diethylene glycol dibenzoate, chemically very similar to the substance identified by infrared analysis, and one with a substantially indistinguishable IR spectrum.

A literature search on diethylene glycol dibenzoate reveals it to be a clear liquid with chemically stable properties and a very high boiling point. It is slightly soluble in water and very soluble in polymers. It is used as a plasticizer for PVA homopolymer and copolymer emulsions, due to its excellent compatibility with polyvinylacetates and polyvinyl chloride. It is also used for PVC coatings, food packaging adhesives and paints. It can be used as a plasticizer in the cosmetics industry. There may be regulatory issues regarding these uses and the disposal of materials containing this material because of its apparent toxicity as indicated by testing on rodents.

In further analysis the TG-IR showed that between 300 and 450 °C the polymer in the sample decomposes releasing acetic acid, as shown in the graph below; the polymer in the sample is therefore very likely polyvinyl acetate:

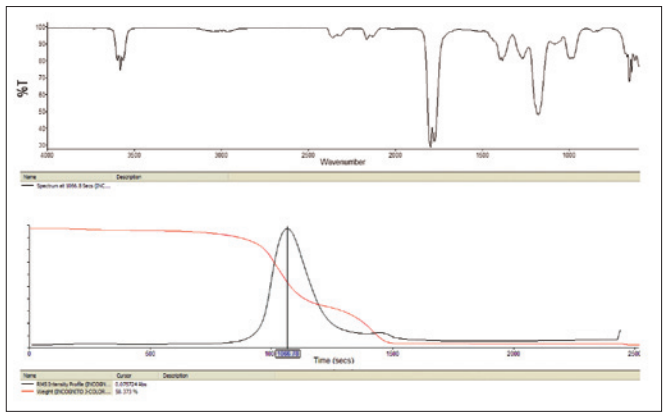


Figure 8. The IR spectrum (upper plot) taken at the peak rate of weight loss (lower plot) of the first stage of the decomposition of the polymer substrate of the analyzed film.

Summary

The use of "hyphenated techniques", TG-IR and TG-GC-MS, which link separation and identification instrumentation, together with search software and established research data bases has enabled an unknown aqueous mixture to be effectively analyzed and its components identified.

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