APPLICATION NOTE

Evolved Gas Analysis

AUTHOR

Greg Ainsworth
PerkinElmer, Inc.
SeerGreen, UK

Evolved Gas Analysis for the Identification of Paint Components

Introduction

Paints contain a variety of components including pigments, fillers, binders, solvents, and additives, each having a particular function within the product. A variety of organic and inorganic compounds can be used in their formulation. Due to the complex nature, the multiple components and the high viscosity of most paint formulations, there are a number of challenges for most analytical techniques used for paint analysis that often limits the technique to partial analysis, such as solvent analysis by GC or GC-MS. An FTIR (Fourier-transform infrared) combined with an integrated sampling module for evolved gas analysis allows for the analysis of all of the components present in a paint formulation.

The PerkinElmer EGA 4000 is a world first that combines both thermogravimetric analysis and infrared spectroscopy into a unique, fully integrated, in-sample-compartment module. The control of the EGA 4000 is fully integrated into the Spectrum 10 software allowing the complete experiment to be conducted within a single software platform.

PerkinElmer®
For the Better

Experimental

The PerkinElmer Spectrum 3™ and the EGA 4000, shown in Figure 1, were used for a series of experiments on two different paint types; a solvent-based and an aqueous-based.

The use of these combined techniques allows for the identification of the materials present from the FTIR spectra obtained and a whole host of information from the TGA (Thermogravimetric analysis) weight loss curve.

Figure 2 shows a typical weight loss curve with three distinct weight losses when the sample is heated from room temperature up to 700 °C. The first of these is where volatile compounds such as solvents will evolve. The second stage is where the bulk of the material will thermally breakdown. The third stage is a combustion stage where any residual soot/carbon will be burned off in an air or oxygen purge gas. Any weight remaining at the end of the experiment will be a solid residue, typically inorganic, of a filler or pigment. This can be retained and later identified using an ATR (Attenuated total reflectance) accessory.

Figure 1: PerkinElmer Spectrum 3 with the EGA 4000 Accessory.

Solvent Loss Experiments

After a paint is applied to a surface it will lose the solvent and other volatile materials over a period of time. The rate of solvent loss will vary with temperature until ultimately all of the solvent will have evaporated. The solvent content can be determined from the TGA curve by the amount of weight loss. Two experiments were performed for each of the two paints, both using hour long isothermal periods at the two different temperatures of 30 °C and 50 °C.

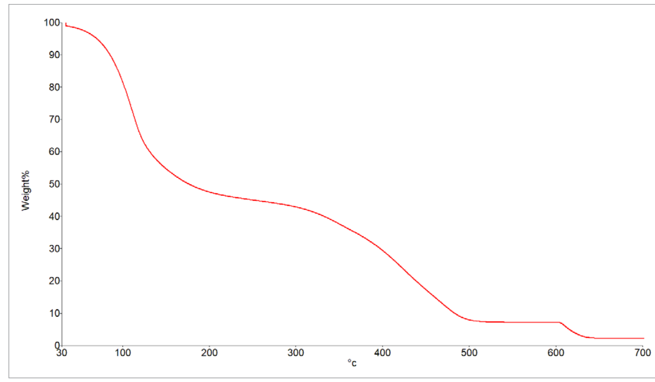

Figure 2: Typical Weight Loss Curve.

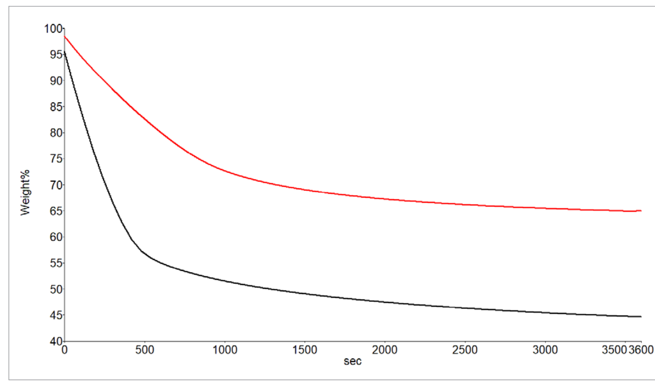

Figure 3: Weight Loss Curves for the Solvent-Based Paint at 30 °C (Red) and 50 °C (Black).

It can be seen from this data that the solvent evolves at a much faster rate when the sample temperature is 50 °C and at 30 °C the solvent is still evolving even after a one hour time period. In the experiment at 50 °C a small proportion of the solvent is lost immediately when the sample is placed in the hot furnace environment. Ultimately (but not shown in this data), in both experiments the weight loss due to the solvent corresponds to approximately 50% of the sample. This weight loss can be accurately determined if required.

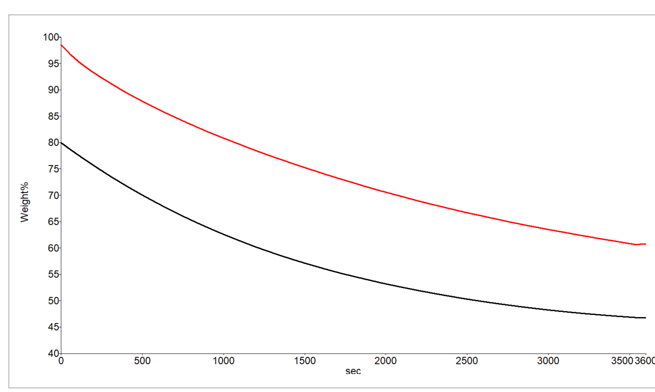

Figure 4: Weight Loss Curves for the Acrylic-Based Paint at 30 °C (Red) and 50 °C (Black).

The aqueous-based paint sample, an acrylic, shows similar trends in the data. The weight loss occurs at a much faster rate when the sample is at 50 °C than at 30 °C and in both cases the "solvent" evolution is incomplete after an hour. Again, the "solvent" accounts for approximately 50% of the sample weight loss.

Further experiments were then performed where the experiments were extended to heat the samples up to 700 °C, enabling the detection of other volatiles and the determination of other materials present in the formulations. Experimental setup and data collection was all performed using the Spectrum Timebase software.

Acrylic Based Paint

The results obtained from the acrylic-based paint experiment are shown in Figure 5. The results shown are the weight loss curve and the Gram-Schmidt plot (an indication of total IR absorbance for each spectrum recorded).

At various points during the run, it can be seen that there are different IR spectra due to the different evolving gases. The following section details the gases evolved from this sample.

The first spectrum obtained is shown as Figure 6 and is clearly the spectrum of water vapor.

The next gas that starts to evolve at about 130 °C is shown in Figure 7a and has been identified as propylene glycol as shown in the results table (Figure 7b).

The next different gas evolved at around 235 °C which the library search identified as 4- Methylbenzenesulfonamide as shown in Figure 8.

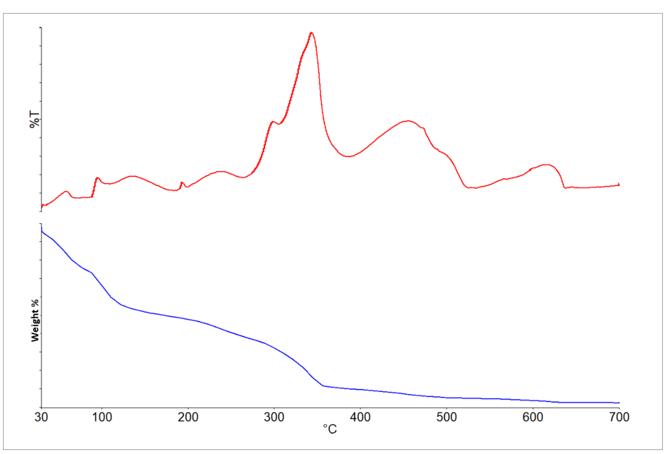

Figure 5: Gram-Schmidt plot (top) and Weight Loss curve (bottom) for acrylic paint sample.

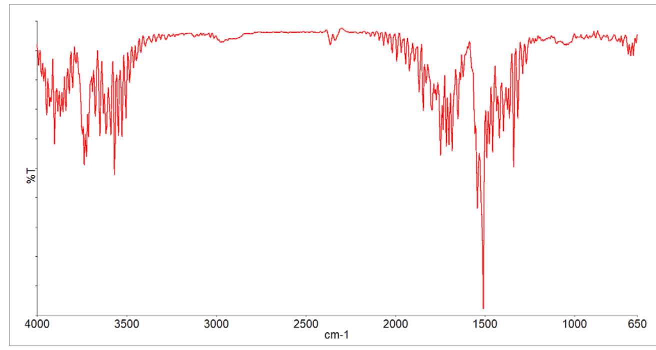

Figure 6: Spectrum showing the evolved water vapor.

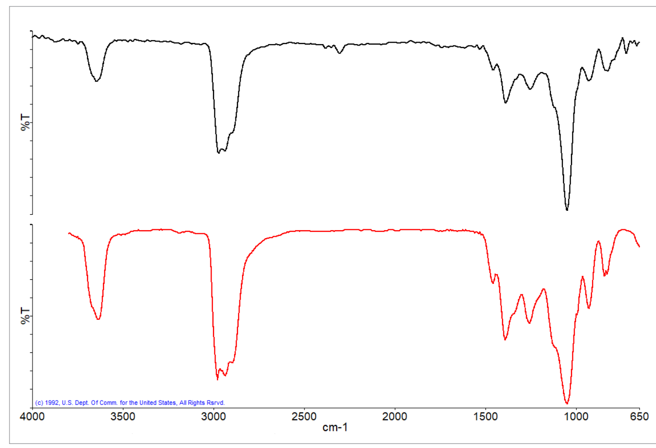

Figure 7a: Spectrum measured at 130 °C (black), best match library spectrum (red).

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.896456	V00030.SP PROPYLENE GLYCOL, 57-55-6
2	0.843833	HR353.SP PROPYLENE GLYCOL AT 25 C, COMPOSITE SPECTRUM (1 PPM-METER AT 2

Figure 7b: Search Results of the spectrum at 130 °C showing Propylene Glycol as the best Match.

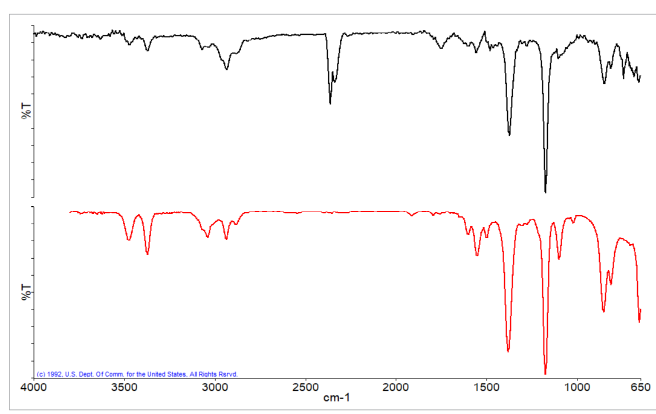

Figure 8a: Spectrum measured at 235 °C (black), best match library spectrum (red).

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.922985	V00070.SP BENZENESULFONAMIDE, 4-METHYL-, 70-55-3
2	0.911165	V00301.SP BENZENESULFONAMIDE, 2-METHYL-, 88-19-7

Figure 8b: Search Results of the spectrum at 235 °C showing 4-methylbenzenesulfonamide as the best Match.

The major weight loss in this experiment, due to the breakdown of the main component, peaks at around 345 °C. The IR spectrum obtained, shown in Figure 9, was searched against spectral libraries and identified as methyl methacrylate

This is commonly used as a binder to help form the emulsion of the paint.

The thermal breakdown of the main polymer system in the paint is likely to generate some carbon in the form of soot. In the presence of air in the purge gas this will convert the carbon into carbon dioxide at higher temperatures leading to a weight loss and carbon dioxide spectra observed.

After the combustion of the carbon a residue was left in the sample pan that could be scanned using an ATR accessory the spectrum of which was then also searched using reference libraries to try to identify the material present. The ATR spectrum of the residue is shown as Figure 10 with the best library match being Anhydrite, an inorganic mineral.

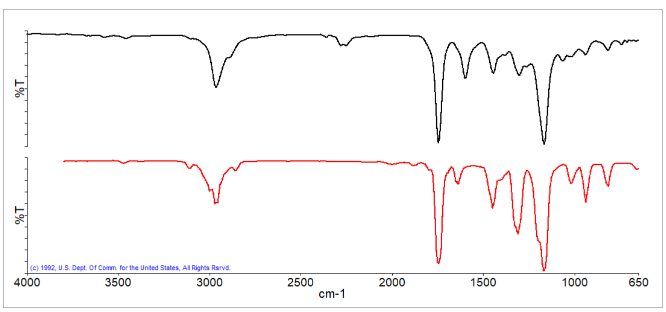

Figure 9a: Spectrum measured at 345 °C (black), best match library spectrum (red).

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.897495	V00225.SP 2-PROPENOIC ACID, 2-METHYL-, METHYL ESTER, 80-62-6
2	0.885403	V01911.SP FORMIC ACID, BUTYL ESTER, 592-84-7

Figure 9b: Search Results of the spectrum at 345 °C showing Methylmethacrylate as the best Match.

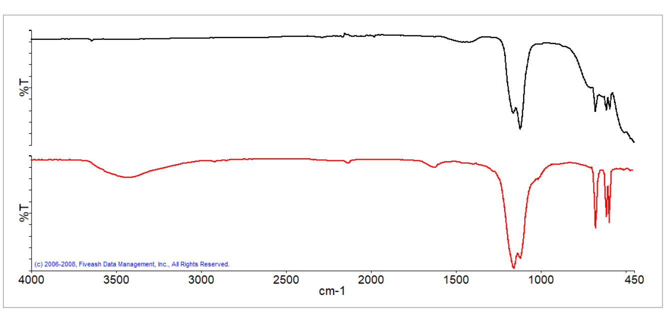

Figure 10a: ATR Spectrum of the residue(black), best match library spectrum (red).

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.824098	M012.SP ANHYDRITE IN KBR (TREATED AT 1000 DEGREES CENTIGRADE), FRANCE:
2	0.721087	M049.SP GYPSUM IN KBR, VERMONT: H & S 333B
3	0.702647	M048.SP GYPSUM IN KBR, ITALY: H & S 26B

Figure 10b: Search Results showing Anhydrite as the best match when compared to the collected Spectrum.

Solvent Based Paint

The results obtained from the solvent-based paint experiment are shown in Figure 11. The results shown are the weight loss curve and the Gram-Schmidt plot (an indication of total IR absorbance for each spectrum recorded).

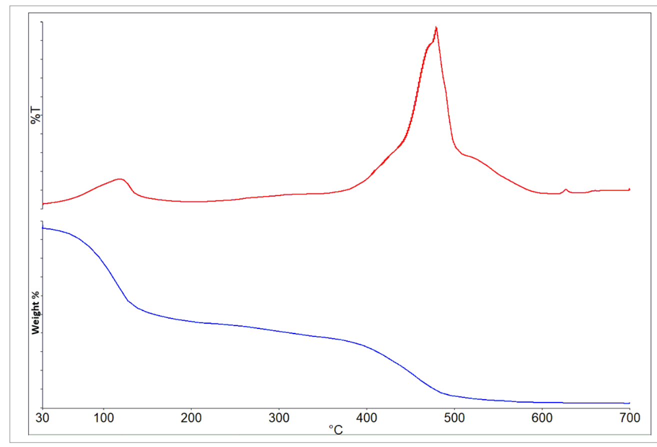

Figure 11: Gram-Schmidt plot (top) and Weight Loss curve (bottom) for the solvent-based paint.

It can be seen from the data that there are two major weight losses at about 110 °C and 460 °C, but also a broad weight loss between 250 - 350 °C. The first weight loss corresponds to the loss of solvent and generates the IR spectrum shown in Figure 12.

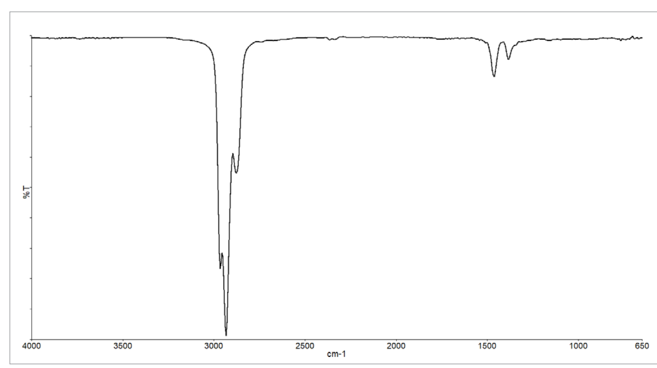

Figure 12: Spectrum from the weight loss at 110 °C.

The solvent used in the paint was identified to be hydrocarbon. However, IR is not able to definitively determine the hydrocarbon chain length and it is also possible that mixed hydrocarbons were used.

The broad weight loss event occurring between 250- 350 °C generates the spectrum shown in Figure 13a, and the material has been identified using a library search (shown in Figure 13b) as phthalic anhydride.

Phthalic acid is often used in solvent-based paints as it forms the alkyd resin, acting as the film-forming component allowing it to form a proper coating onto a surface.

The final weight loss is due to the loss of carbon (soot) residue from the breakdown of the components in the paint system.

After the temperature program had completed the IR spectrum of the residue from the pan (shown in Figure 14) was scanned using the ATR accessory and searched against reference libraries.

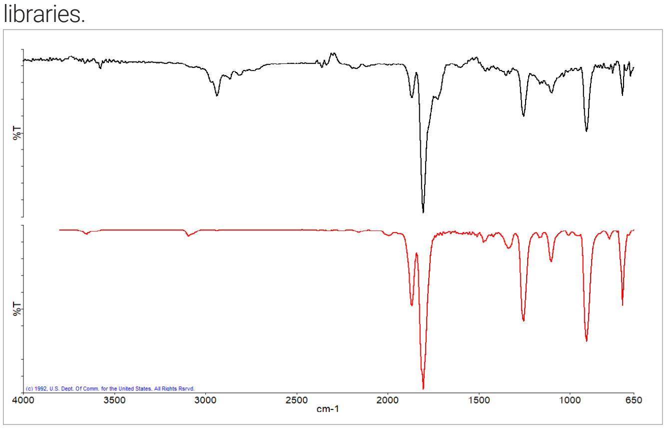

Figure 13a: Spectrum from the weight loss between 250 - 350 °C (black) and the best library match spectrum (red).

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.938228	V00252.SP PHTHALIC ANHYDRIDE, 85-44-9
2	0.92094	V03310.SP 1,2-BENZENEDICARBOXYLIC ACID, MONO(PHENYLMETHYL) ESTER, 2528-

Figure 13b: Search results for the spectrum collected between 250 - 350 °C identified as Phthalic Anhydride.

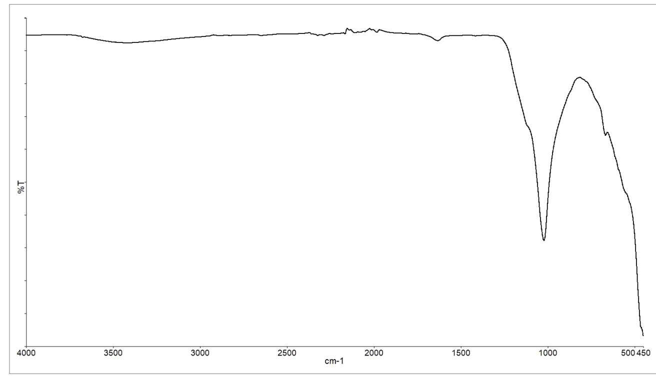

Figure 14: ATR Spectrum of the residue from the solvent paint.

The material is an inorganic compound; however, the spectral search did not give a definitive identification most likely due to the compound not being present in any of the spectral libraries used for the search.

Conclusions

The combination of the two techniques of thermogravimetric analysis and infrared spectroscopy possible using the EGA 4000 has proven to be an effective way to identify the components present in each of the different paint formulations. The experiments have shown that it is also possible to determine the relative amounts of the components based on the individual weight losses, including solvent content and residual solids. The ability to swap between ATR and the EGA 4000 on the Spectrum 3 offers a whole range of analysis possibilities for the paints industry.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

920744 PKI