

## Thermogravimetric Analysis – Infrared Spectroscopy



## Characterization of Soil Pollution by TG-IR Analysis

There are many scenarios in which soil can become contaminated by hydrocarbon products. Leakage from fuel storage tanks or transfer lines as well as storm water runoff from vehicle washing areas are just two examples. In environmental monitoring or land reclamation, therefore, it is important to test soil for contamination. Total petroleum hydrocarbon (TPH) testing by solvent extraction and infrared spectroscopy is a sensitive method, but has a considerable burden of sample preparation. A gas chromatographic analysis of the extract can provide even greater sensitivity and more detailed compositional information, but further increases the time required for the analysis.

Thermogravimetric analysis coupled to infrared spectroscopy (TG-IR) can provide detailed information about the amount and nature of the pollution, while requiring no sample preparation at all. This application note illustrates the kind of data that can be obtained with a modern TG-IR system.

### Experimental

A soil sample was obtained and mixed with diesel fuel at a concentration of about 10% m/m. 17 mg of the soil was transferred to the crucible of a PerkinElmer® TGA 4000, coupled to a PerkinElmer Spectrum™ 100\* infrared spectrometer by the TL 8000 transfer line with a 10-cm gas cell. The transfer line and gas cell were heated to 280 °C to avoid any risk of condensation of heavier organic compounds. The purge gas through the TGA was nitrogen at flow rate of 20 mL/min with a balance purge of 40 mL/min. This combined rate of 60 mL/min was kept constant through the transfer line and cell. The temperature was increased from 30 to 800 °C at a constant rate of 20 °C/min. Infrared spectra over the range 4000–600  $\text{cm}^{-1}$  were collected every 12 s at 8  $\text{cm}^{-1}$  resolution (co-adding four interferometer scans for each spectrum). Pyris™ software was used to control the TGA, while TimeBase™ was used for collection and analysis of the time-resolved IR data.

\* The PerkinElmer Frontier FT-IR supercedes the Spectrum 100. The TG-IR interface is compatible with the frontier, and delivers equivalent performance.

## Results and Discussion

The weight-loss curve for the soil sample is shown in Figure 1. Broadly, there are three significant, overlapping weight loss events: the first begins just above ambient, the second begins at around 100 °C and continues until 250 °C, and the third begins at around 250 °C and is nearly complete by 600 °C. At 700 °C, approximately 65% of the soil mass remains unburned, and this can be assumed to consist of inorganic material.

The average intensity of the IR absorption is depicted by the Gram-Schmidt thermogram, plotted against the weight and derivative weight curves in Figure 2. The instantaneous concentration of absorbing components in the evolved gas sampled by the IR is proportional to the rate of weight loss (among other factors) and, accordingly, a strong correspondence is seen between the Gram-Schmidt thermogram and the derivative weight curve.

Results from the selected wavenumber regions of the IR measurements are shown in Figure 3 (Page 3), and provide rich information about the processes occurring during the analysis. At temperatures slightly above ambient, an increase in water vapor is seen, indicating that the soil was not completely dry. This accounts for the first weight loss of 5% on the TGA plot. The first peak in the Gram-Schmidt thermogram occurs at about 230 °C and is related to the second weight-loss event. Inspection of the spectrum (Figure 4 - Page 3) reveals that this is due to a mixture of water vapor, aliphatic hydrocarbons, and, from the peak at around 1745  $\text{cm}^{-1}$ , an ester. This suggests that the contaminant may be diesel fuel with a significant fraction of biodiesel (fatty acid methyl esters).

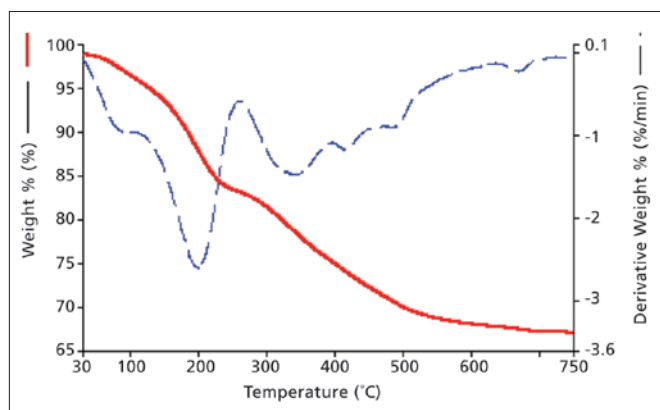


Figure 1. Weight loss (solid red line) and derivative (dashed blue line) for the contaminated soil sample.

The ester peak is overlapped by water-vapor absorption, but there is another selective peak for biodiesel at around 3015  $\text{cm}^{-1}$ , corresponding to an alkene C-H stretching mode arising from unsaturation in the fatty-acid chains. Plotting the intensity of this peak as a function of temperature (Figure 3) reveals that the peak occurs slightly later, at around 240 °C. The 10% weight loss seen in this temperature range is in agreement with the known diesel concentration. This indicates that the TGA-IR measurements can provide an estimate of the amount of contamination present, as well as detailed information about the composition.

At higher temperatures, the main gases evolved are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , as organic matter in the soil undergoes combustion. This accounts for the final weight-loss event.

TimeBase also allows the series of spectra to be plotted as a stack or as a surface in a three-dimensional plot, as shown in Figure 5. This gives an excellent overview of the complete dataset, and the evolution of the absorption features with time can be seen at a glance.

A reference diesel/biodiesel blend sample was also analyzed by TG-IR under the same conditions as the soil sample. The results are presented in Figures 6 and 7 (Page 3). The entire sample has evaporated by 300 °C. In Figure 7, it can be seen clearly that the biodiesel evaporation lags behind that of the fossil diesel. There is no water in the diesel standard sample, so the carbonyl absorption can be followed directly. This data gives confidence that a biodiesel/diesel blend is indeed the contaminant present in the soil sample.

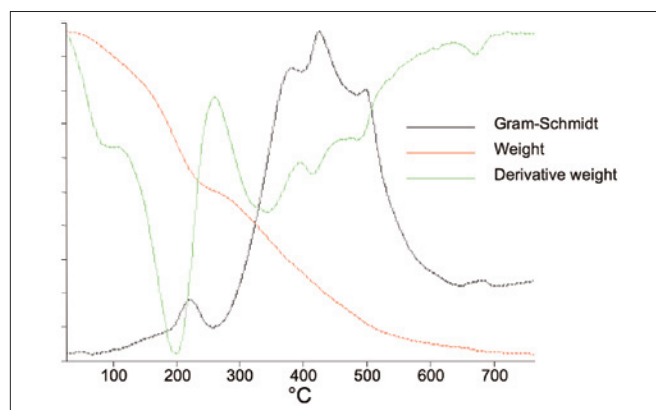


Figure 2. Weight (red), derivative weight (green), and Gram-Schmidt thermogram (black) plots for the contaminated soil sample.

## Conclusions

Thermogravimetric analysis gives valuable quantitative information about the sample, but has limited ability to identify materials. Infrared spectroscopic analysis of the evolved gas provides precisely this capability. This note demonstrates that not only is TG-IR capable of determining the quantity of diesel present in soil, but the minor fraction of biodiesel in the fuel could also be detected. For soil analysis, a key advantage of TG-IR over other methods is that no sample preparation or solvent extraction step is required, giving a much faster and more convenient analysis.

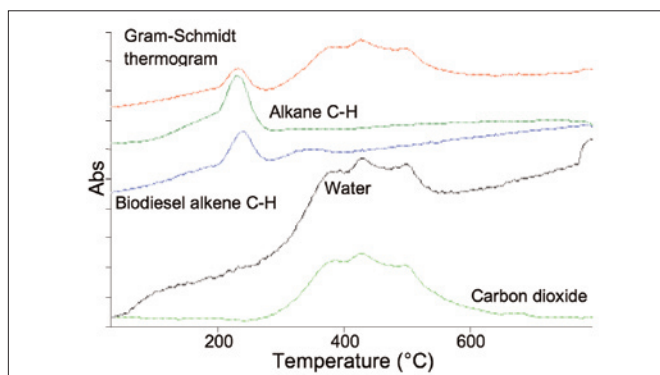


Figure 3. Temperature-based absorbance profiles for the contaminated soil sample. Red: Gram-Schmidt thermogram showing the overall absorption intensity; Dark green: height of the C-H absorption around 2933  $\text{cm}^{-1}$ , corresponding to aliphatic hydrocarbons (diesel and biodiesel); Blue: height of the alkene C-H absorption around 3015  $\text{cm}^{-1}$ , corresponding to unsaturation in the biodiesel; Black: height of the water absorption between 3800–3700  $\text{cm}^{-1}$ ; Light green: height of the carbon dioxide peak around 2370  $\text{cm}^{-1}$ .

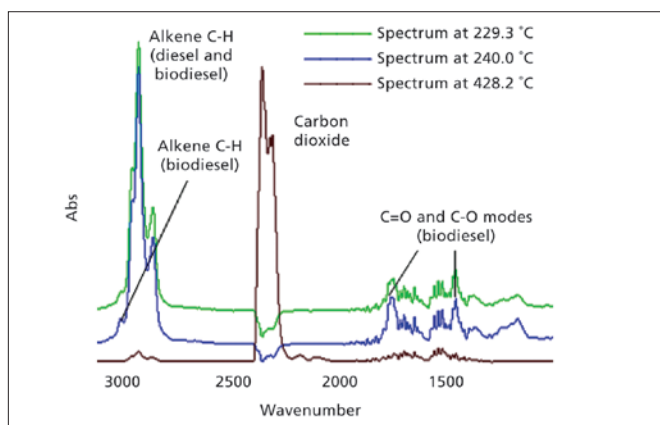


Figure 4. Selected spectra from the TG-IR analysis of the contaminated soil sample.

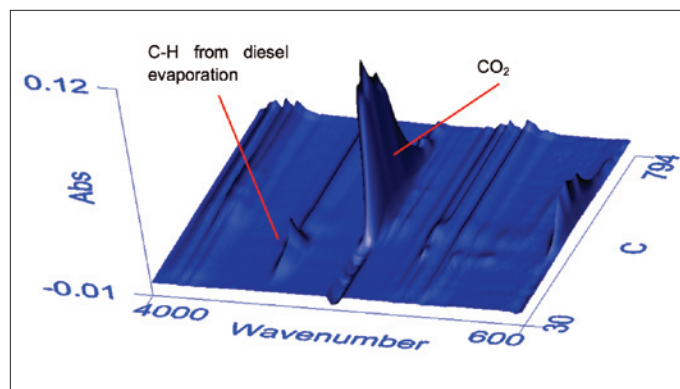


Figure 5. Three-dimensional plot of the time-resolved spectra for the contaminated soil sample.

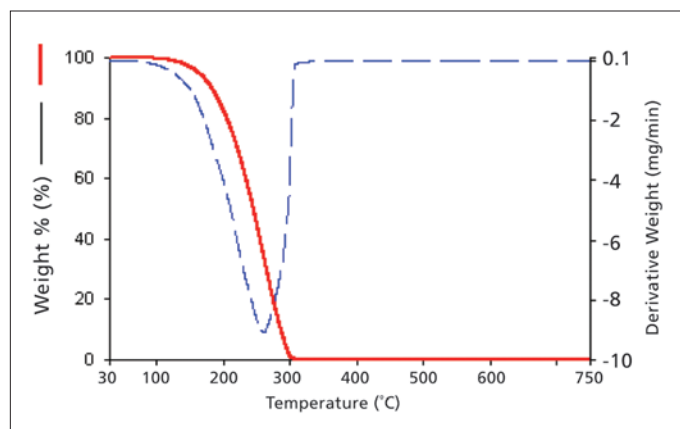


Figure 6. Weight-loss (solid red line) and derivative profile (dashed blue line) for the biodiesel blend standard sample.

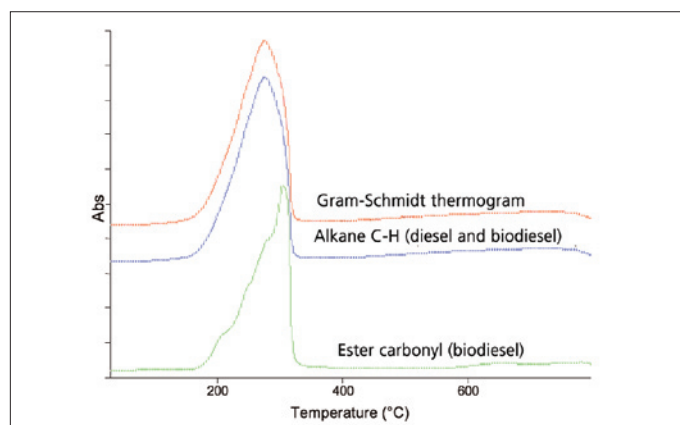


Figure 7. Temperature-based infrared absorption profiles for the biodiesel blend standard sample. Red: Gram-Schmidt thermogram; Blue: height of the C-H absorption around 2933  $\text{cm}^{-1}$ ; Green: height of the ester carbonyl absorption around 1745  $\text{cm}^{-1}$ .