

Doing the Dirty Work: Combined TGA-IR and Transmission Studies of Soil

Key Words

- Ammonia Doublet
- Forensic Analysis
- Pyrolysis
- TGA-IR
- Trichlorobenzene (TCB)

Introduction

Professionals in the fields of forensics, pollution remediation, and agriculture frequently analyze soils. Several aspects of soil are of interest, including the inorganic and organic content. The former is typically analyzed by elemental methods (AA or ICP). The “total organic” content is measured in most cases by mass loss upon pyrolysis. Essentially, the soil is weighed, heated in air to a high temperature, and reweighed upon cooling. The weight loss is (assumed to be) due to loss of organic content. This method alone does not identify the organic material, it only gives a value for the total organic content.

Cox, et al.¹ have described an FT-IR forensic analysis of soil. The basic method involves subtracting transmission spectra before and after pyrolysis. The “missing peaks” represent organic material removed during heating. The method is simple to implement, and gives far more information than mass loss alone. However, there is also an opportunity to acquire information about the organics by analyzing the off-gassing material during the heating step.

This application note describes how TGA-IR can extend the capabilities of the pyrolysis procedure. TGA-IR combines features of both previous experiments (pyrolysis weight loss and IR difference), but also captures potentially useful information about the gases emitted during the heating step.

In a thermo-gravimetric analysis (TGA), a sample is heated and the weight loss is determined using a micro-balance. The gases driven off can be fed into a gas transmission cell in an FT-IR for identification during the TGA run. This can add qualitative information to the quantitative TGA data. The TGA-IR method is commonly used in failure analyses of rubbers and polymers and in analysis of museum display materials.²

Procedure

A Thermo Scientific Nicolet™ Series FT-IR spectrometer was used to collect transmission data on KBr pellets, and TGA data using the TGA interface accessory. The combined TGA-IR unit is shown in Figure 1. The transmission spectra were collected using 32 scans at a resolution of 4 cm⁻¹. The Thermo Scientific OMNIC™ Time Series software was used to collect the time-series data during the TGA experiment. 6 scans at 4 cm⁻¹ resolution were collected, giving a time resolution of about 7.8 seconds. Both the spectrometer and the TGA were purged with nitrogen or dry air.

Two soil samples were obtained from garden plots. One sample was split into two batches; 250 microliters of 1,2,4-trichlorobenzene (TCB) was added to 50 grams of soil from one of these batches. The EPA notes TCB is an important pollutant

tracked in drinking water, having been used as an insecticide and other applications.³ TCB was chosen as a contaminant because, as the EPA notes, TCB binds well to soil. The TCB containing sample was treated the same as the other samples throughout.

The soil samples were initially dried for about an hour at 100 °C. The clumps were then gently ground, and fed through a coarse sieve, to remove rocks, sticks and other macro organic particles. About 250 mg of this material was then dried more thoroughly.

100-130 mg of the dried soil was placed in a platinum TGA pan. The samples were heated at 20 °C per minute from ambient to either 650 or 800 °C. The mass loss was measured directly by the TGA. Samples were recovered from the TGA and placed into sealed centrifuge tubes.

About 200 mg of KBr was mixed in a mortar and pestle with between 10 and 15 mg of the soil (both before and after heating). Half of this mixture was placed into a 7 mm die and then pressed to 8 tons pressure. The resulting pellet was highly transparent. No quantitative measurements were attempted.

Results

The TGA results are very clear and the signal to noise very high, even with the small number of scans taken. Most spectra show considerable water and CO₂ from the breakdown of other organic matter. A snapshot of the TGA results for the spiked (TCB) sample is shown in Figure 2. The contaminant peaks are clearly seen, and the identity of the contaminant can be determined via searching. Extracted single spectra (6 scans) from contaminated soils dried a short time and a longer time are shown in Figure 3, along with the vapor phase spectrum for TCB. These spectra were taken at after 10 minutes, so the oven temperature was around 240 °C.



Figure 1: The Thermo Scientific Nicolet iS™ 10 FT-IR spectrometer with the TGA accessory inserted

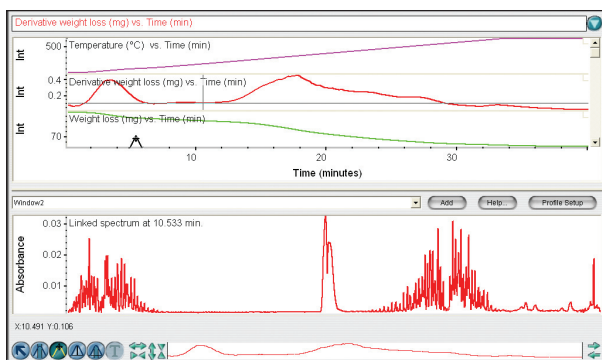


Figure 2: View of the OMNIC Time Series software, showing data for a TCB contaminated sample at a low temperature

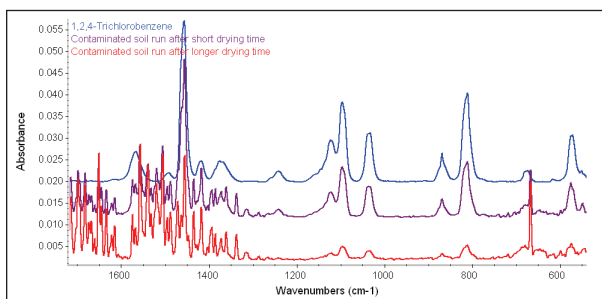


Figure 3: Search result for TCB shown against single time point evolved gas spectra from two contaminated soils. The series of peaks at 1550 cm^{-1} are water, and the peak at 675 cm^{-1} is CO_2 .

The primary signal seen for all the samples were water and carbon dioxide. A doublet due to ammonia is one feature seen in all samples.⁴ Figure 4 shows this for the most pronounced ammonia signal, found in the sample from a yard where a family pet was kept. This intriguing and slightly humorous observation would need more experiments to confirm. Nitrogen in the soil is an important constituent, regardless of origin, so this feature indicates where the additional data obtained from the TGA experiment has great benefit. Ammonia is generated from all of the samples in some quantity, regardless of which carrier gas (nitrogen or dry air) was used. The TGA data shown at the top of Figure 2 (weight loss and derivative weight loss) indicates the amount of mass being lost at the higher temperatures is very small compared with that lost earlier (mostly due to moisture), so the nitrogen being expelled is quite low. The detection of ammonia even at the low concentrations shows the sensitivity of the TGA-IR method. With careful calibration, this may enable the experimenter to determine the nitrogen content of the soil independently.

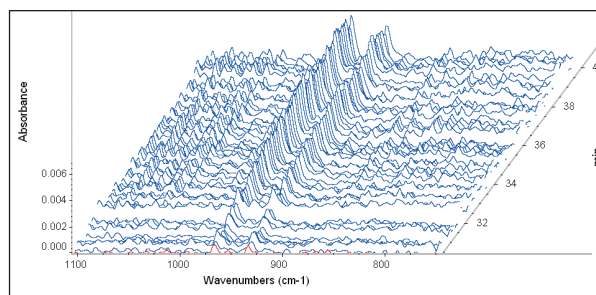


Figure 4: Waterfall plot showing the ammonia peak generated from a soil sample

The paper by Cox, et al.¹ reported a maximum pyrolysis temperature of 650 $^{\circ}\text{C}$. The spectra in Figure 5 show the transmission results for the contaminated soil run before and after treatment to 650 and 800 $^{\circ}\text{C}$. There are not strong differences between the soils run to the different maximum temperatures, but both the TGA data and the IR data does show an additional “hump” of weight loss in all these samples at temperatures above 650 (data not shown here).

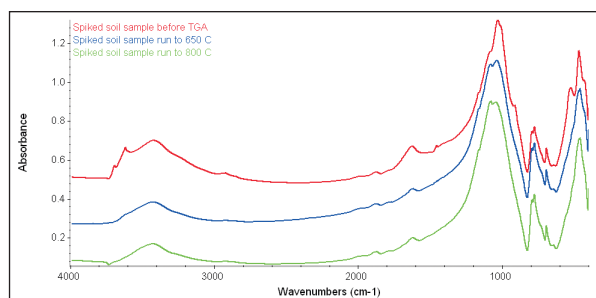


Figure 5: KBr pellet transmission data for the contaminated soil before and after treatment

Conclusion

The Nicolet Series of FT-IR spectrometers coupled with the TGA accessory have a high sensitivity for use in analyses of this kind. The high quality of the TGA data shown here confirm this unit has the responsiveness needed for the TGA experiment, and should lead to development of many new applications in this vein.

The analysis of soil using the combined TGA-IR and transmission experiments provides some tantalizing new insights into the analysis of soils. The ability to extract information about contaminations should lead to developments in the field of remediation, while the possibilities for determining the nitrogen content are just beginning to be explored.

References

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3. <http://www.epa.gov/ttn/atw/hlthef/tri-zene.html>
4. Thermo Fisher Scientific Applications Note AN50753_E 07/04M

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