AFR

The TG/Plus System Integrates The DuPont 951 TGA With The Bomem M-100 FT-IR Spectrometer

The TG/plus system, jointly developed by Advanced Fuel Research, Inc. (AFR) and Bomem Inc., is a full-featured, easy-to-use, integrated thermogravimetric (TG) Fourier Transform Infrared (FT-IR) system. The instrument is composed of a Michelson 100 FT-IR spectrometer, a DuPont 951 thermogravimetric analyzer (TGA), and an IBM™ compatible computer. Offering a complete TG to FT-IR interfacing, the TG/plus makes the analysis of plastics, coal, source rock, paper, catalysts, textiles and many other materials easy.
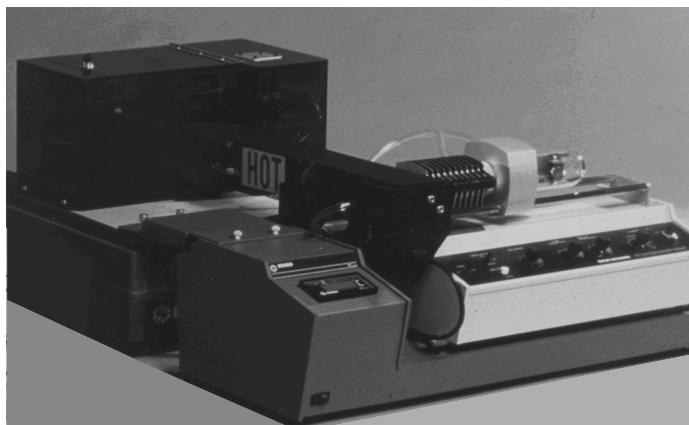
A Unique Real Time Quantitative Analysis of Evolving Products

The TG/plus quantitative analysis routine relies on a database of calibration spectra to which additional spectra can easily be added. The routine decides which regions of each calibration spectrum to use for the best quantitation with the least interference. Integration windows can also be used to follow unknowns or specific functional group absorptions. Up to 20 species can be quantitated at one time.

Gas-evolution patterns during pyrolysis of a Zap Indianhead Lignite coal are shown in Figure 1. The weight loss resulting from pyrolysis of this coal is shown on the front cover. The sample was first heated to 150°C at 30°C/minute in helium, and held there for a few minutes for drying. Then it was heated to 900°C at the same rate. After cooling to 250°C, oxygen was introduced and the sample was heated to 700°C at 30°C/minute to oxidize.

The TG/plus curves shown in Figure 1 (below) indicate the amount of H_2O, SO_2, volatile hydrocarbons (tars and CH_4), and oxidized species evolving from the sample at any given time during the experiment.

The first species to evolve is the moisture initially present in the sample. Upon further heating, a myriad of reactions occur:

- minerals release SO_2 and CO_2 throughout the temperature range
- carbon–carbon bonds in the hydrocarbon structures start to homolytically cleave around 400°C leading to the release of high molecular weight tars
- cleavage of ether linkages contributes to CO production
- CH_4 evolution occurs when hydrogen-scavenging methyl groups are released by carbon-carbon bond breaking or radical displacement reactions.

During oxidation, which is implemented by adding air to the inlet gas, the carbon, hydrogen, nitrogen, and sulfur remaining in the char are converted to their gaseous oxides, as illustrated by the CO_2 evolution in Figure 1. These species are then detected as they flow through the gas cell.

The TG/plus curves on the front cover are integrals of the corresponding evolution curves, and they have been plotted in a cumulative manner from 100% down. Total gas determinations are consistent with those determined by standard ASTM techniques, GC measurements, direct condensation and weighting (tars), and elemental analysis (of char before oxidation).
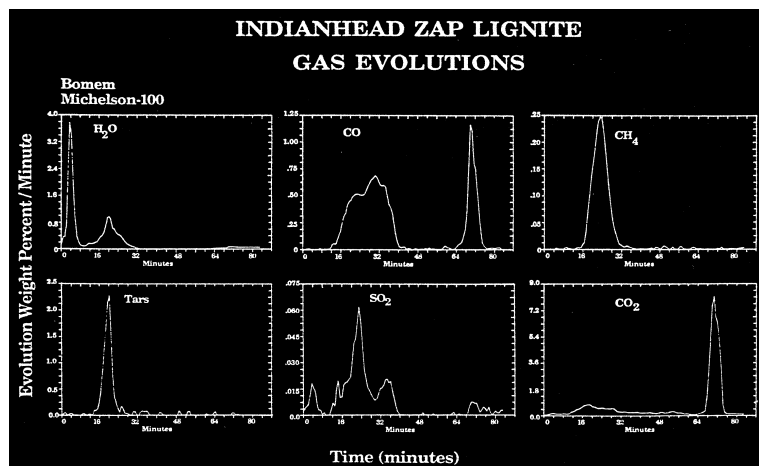

Figure 1.

Real-Time Display

As shown in Figure 2, TG/plus continually updates the screen with weight loss and temperature data, as well as with quantitative evolution and integral weight-loss curves for as many as four species. The TG/plus screen shows the user-defined temperature profile in the top left window. A second curve overlaying this profile is the actual reading from a thermocouple situated near the sample. Information about the weight loss is presented in the balance window (top right) which shows the sample weight loss during the experiment as a percentage of the initial weight. The three basic weight-loss regimes for this sample of Indianhead Zap Lignite are: first, a weight loss from drying, then volatilization as the sample is heated to $900^{\circ}C$, and finally a weight loss as the remainder of the sample is oxidized.

For each of the gases that are displayed, two curves are presented, as shown in the four bottom panels of Figure 2 (right). One curve is the evolution curve, which has the units of weight percent per minute on the y-axis. The second curve is the integral of this evolution.
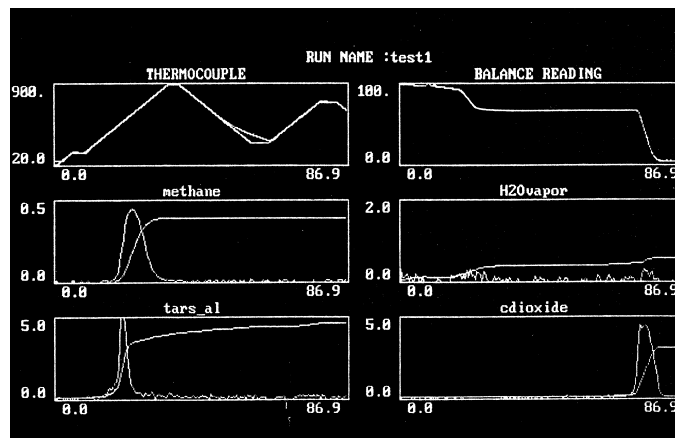

Figure 2.

Analysis of Evolved High Molecular Weight Aerosols

Some difficult to analyze products are the heavy decomposition products which condense at room temperature. These condensates, such as tars from coals or oligomers from polymers, are invariably the major evolved products. The unique design of TG/plus causes these products to condense to a sub-micron aerosol which follows the gas flow into the IR-cell. The particle size of the mist is such that Rayleigh scattering is minimal and the infrared information of the condensate is still quantitative.

Figure 3 (below, left) shows the infrared absorbance spectra of high molecular weight condensables evolving from a polyurethane sample at two different times in the TG/plus heating cycle. Polyurethane foam was heated at $30^{\circ}C$/minute in the TG/plus, and two major weight losses occurred. The first weight loss took place at around $300^{\circ}C$, and the second one at around $420^{\circ}C$. The TG/plus infrared absorbance spectra corresponding to those times can be used to identify the evolving components. The $300^{\circ}C$ temperature spectrum represents a simple nitrile, such as acetonitrile, but it may also have some alkyl groups attached. The $420^{\circ}C$ spectrum is characteristic of a simple aldehyde, such as acetaldehyde. Apparently, the urethane decomposes such that cyanide-bonded species are the first to volatilize. Later, carbon-oxygen bonds in the residue can cleave, and aldehyde structures evolve.

Normally the high molecular weight species can condense and re-pyrolyze, even in heated transfer lines, but with the TG/plus they are carried directly through to the IR gas cell.
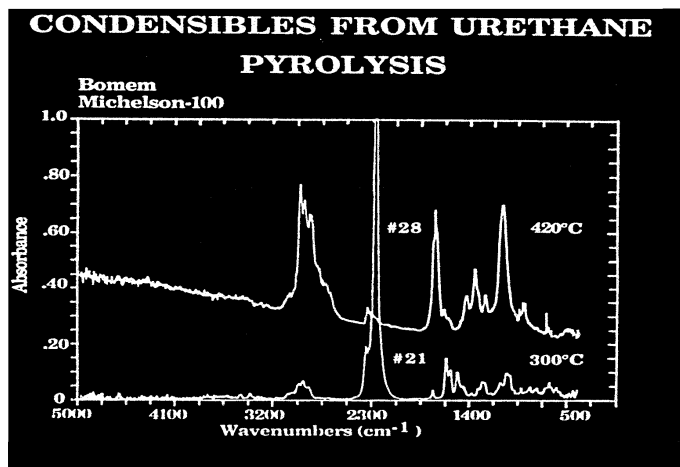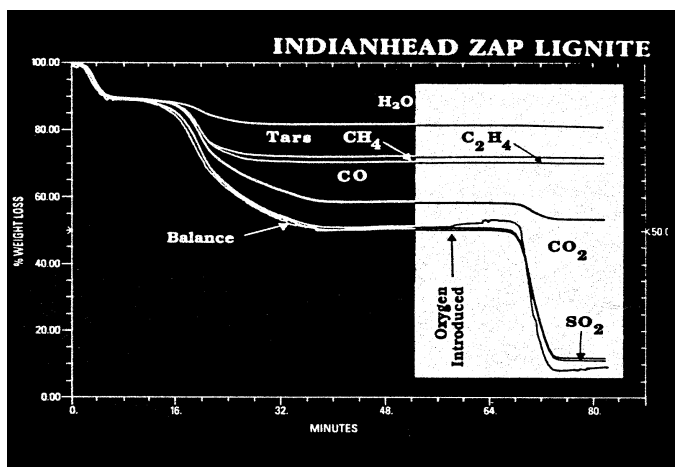

Figure 3.

Figure 4.

Automatic Oxidation Cycle

The TG/plus allows oxygen to be introduced to the sample at selected times for sample oxidation and/or elemental analysis, as shown at the 52 minute mark in Figure 4. The combination of oxygen with C, H, N, or S produces the corresponding oxide which is detectable in the infrared.

In Figure 4, the oxidation portion of the Indianhead Zap Lignite thermogram illustrates several points about this cycle.

At the point where oxygen was introduced, the balance shows a gain in weight, while the gas evolutions show a slight dip due to creation of oxides of carbon and sulfur. Apparently, the sample is not only absorbing oxygen onto its surface, accounting for the weight gain, but the oxygen is also oxidizing the sample.

Pyrrhotite (F_2S) does not release its sulfur until an oxidation step commences. This can usually be noted as an SO_2 release that occurs just before the formation of CO_2. This lignite sample does not, however, retain much of its sulfur in the char, and the corresponding SO_2 evolution during oxidization is very low. This indicates that this specific coal is more easily cleaned (desulfurized) than a coal that tends to retain sulfur in its char.

The temperature at which a sample starts to oxidize, and the oxides are produced, gives information on sample reactivity. The Indianhead Zap Lignite starts to oxidize very early in the oxidization cycle. Samples of graphite generally will not oxidize until the temperature is greater than $800^{o}C$. Reactivities are a starting point to understanding and predicting how materials behave under combustion conditions at much higher temperatures and heating rates.

The TG/plus quantitative information from the gas evolutions during oxidation also allows us to determine the elemental composition of char. When the oxygen has been turned on, TG/plus only accounts for the mass of the elements lost by the sample, and not for the oxygen present in the evolving oxides. For example, if a char contains 12 mg of carbon which is all converted to 44 mg of CO_2, TG/plus only produces a CO_2 weight loss curve indicating 12 mg lost by the sample. In Figure 4, these amounts of weight loss determined by gas analysis almost add up to the weight loss measured by the balance. The only discrepancy is due to residual oxygen in the char, which cannot be detected except by difference. The remainder of the sample after oxidation is inert ash.

Autocalibration

With the presence of both weight loss and quantitative gas evolution data, good mass balance is achieved. However, for cases where non-quantitative calibration spectra are available, the system can calibrate itself by an algorithm that matches specific parts of the gas evolution data to the weight loss curve and produces calibration factors for these spectra.

One example is coal tars, a very complicated combination of aliphatics, aromatics, hydroxyls, ethers, carbonyls, etc. These high molecular weight tars vary from coal to coal and are a combination of fragments with a large range of molecular weights. Thus, no single calibration spectrum exists for coal tar.

These fragments are all similar to one another in some respects: they all have major infrared functional group absorptions for aliphatic hydrogen, aromatic hydrogen, hydroxyl hydrogen, ethers, carbonyls, etc. One way to quantitate the tars would be to determine calibration spectra for pure aliphatics, pure aromatics, pure ethers, etc. Then the composite spectrum for the tar would be the sum of all these determinations.

It is worth noting that the tar that evolves from any one coal does not change composition very much over the range of its evolution. Aside from being slightly enriched in hydrogen, these tars are representative of the original coal structure. A spectrum that has representative infrared absorptions for all of the above-mentioned functional groups can be used to detect the presence of any one of these moieties.

For quantitating coal tars, as in the Indianhead Zap Lignite shown on the front cover, the tar evolution and integral curves are first calculated using the above mentioned representative spectrum as a calibration spectrum. Then the evolution curves from the experiment are utilized in a calculation that compares them to the derivative of the balance reading and adjusts selected concentrations to match the balance reading more accurately.

Coal tars are not the only place where such an approach is useful. Components for which calibration spectra are not readily available are quite common in pyrolysis of polymers. The unavailability of calibration spectra may be caused by a number of reasons, e.g.:

- the pure components are too dangerous to handle
- it is impossible, or too expensive, to synthesize such pure components
- the species are too short-lived.

Also, copolymers at high temperatures will tend to rearrange their subunits, which upon further pyrolysis can yield a plethora of products.

If the unknown compound has infrared absorption bands, the TG/plus software can track the band intensities. The associated evolution curve obtained can be autocalibrated for weight determination.

Multi-Pass Gas Cell Dynamic Range

A 16 pass gas cell having an optical path length of 7.3 m provides the TG/plus with high sensitivity. This sensitivity, along with the large concentration range of calibration spectra in the database, gives TG/plus a very wide dynamic range of quantitation.

A problem that has plagued infrared measurements is the lack of dynamic range for quantitation. Generally, an absorption feature for a molecule has a concentration range of only two orders of magnitude before nonlinear deviations from the Beer-Lambert law become important. The dynamic range of the multi-pass cell incorporated into the TG/plus is utilized efficiently because the quantitation algorithm is capable of shifting to other absorption bands, or other regions in the same band, for any one gas. This maximizes the system's dynamic range.

For example, CO_2 evolution from different samples in the TG/plus can range anywhere from a few micrograms per minute (for very pure hydrocarbon polymers) to a few hundred milligrams per minute (for oxidation of samples containing mostly carbon). This is a variation of five orders of magnitude! With calibration spectra covering this range of concentrations, the quantitation algorithm uses only the absorptions from spectral regions where deviations from Beer's Law are minimized.

Multi-Pass Gas Cell Sensitivity

The sensitivity of the TG/plus system is dependent on the pathlength of the cell, the light throughput of the cell and the flow rates of the analyzed species. The TG/plus configuration allows volatile species to be analyzed with an optimum sensitivity and still maintain the proper flow of the high molecular weight aerosols. This is very important for the proper analysis of samples such as polyesters, resins, copolymers and polymers containing cross-link sites, coals, tars, and many more difficult to analyze species.

Another consideration in optimized cell design is the time resolution necessary to identify individual evolution events. For example, the evolution of some volatiles from tobacco, or "unzipping" reactions in certain polymers, occur over very narrow temperature ranges. The TG/plus gas flow rates are set to be able to resolve and record these fast gas evolutions.

The gas cell employed in the TG/plus design is a 16-pass cell with a path length of 7.3 m. With this cell, the following gas detection limits can be achieved:

TG/plus DETECTION LIMITS

Species	Gas Detection Limit
Ammonia	0.3 μg/sec
Methane	0.2 μg/sec
Carbon Dioxide	0.15 μg/sec
Carbon Monoxide	0.6 μg/sec
Paraffins	3.0 μg/sec
Acetylene	0.7 μg/sec
Ethylene	0.8 μg/sec
Water	1.4 μg/sec

These detection limits are for a 30-second collection time, with the system operating under standard TG/plus conditions using a room temperature DTGS detector. Other gases will have different detection limits. Optionally, a high sensitivity MCT type detector can be added to the TG/plus system to increase sensitivity even further.

Conclusions

The instrument sensitivity for gas detection is sufficient even for difficult analyses such as:

- Hydrocarbons in source rock
- Contaminants on catalysts
- Sulfur components (SO_2, COS, CS_2) from oil shale and rubber
- HCl from polymers
- Nitrogen species (HCN) from waste oil
- C1–C4 hydrocarbons in coal, chars, and tars
- Aldehydes in wood and lignins
- Nicotine in tobacco and related products

and many more applications yet to be discovered!

For more information, please contact:
Dr. Marek Wójtowicz
Manager, Hydrocarbons Group
at extension 142, or email marek@AFRInc.com

Research & Development, Analytical Services and Consulting in Advanced Sensors, Materials and Fuels