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# Application of TG–FTIR to the determination of organic oxygen and its speciation in the Argonne premium coal samples

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**Abstract**

During rapid pyrolysis of coal, TG–FTIR (thermogravimetry – Fourier transform infrared) technique can be effectively used to simultaneously detect and measure the three main O-containing gases, namely $H_2O$, CO and $CO_2$. Their sum corresponds to the quantitative amount of oxygen in the coal and is, in general, inherently more accurate than the 'by-difference' values.

In this paper, we first attempt to relate the 'by-difference' values for %O reported for the Argonne premium coal samples (lignite to bituminous rank) (Argonne Users Handbook) to those determined from a TG–FTIR examination of the pyrolysis gases evolved. Another objective of the work is to relate the pyrolysis gases ($H_2O$, CO and $CO_2$) evolved to oxygen-containing functional groups found in coals as well as the evolution of these functional groups as a function of rank. Correlations are also developed between the TG–FTIR oxygen values and other parameters determined for the Argonne Premium Coals. In particular, comparisons of our results using TG–FTIR with analyses carried out by other workers on functional group analysis of acidic groups are considered.


*Keywords:* Argonne premium coals; Oxygen content; TG–FTIR; Oxygen functional groups

## 1. Introduction

Knowledge of the amount of organic oxygen in a coal sample is important for many reasons. In coal conversion processes, it has a bearing on the process parameters necessary to obtain high conversion and determines the difficulty of upgrading liquid products to stabilized chemical entities. For coking coals, it may indicate undesirable weathering that will have a negative impact on coke quality. Combustion techniques are commonly used in the analysis of coal and organic compounds in general for the determination of elemental hydrogen, carbon and nitrogen according to ASTM D3176-89 [1]. For oxygen, the method in common practice involves the determination 'by-difference' from directly determined values for moisture, ash, sulfur, hydrogen, carbon and nitrogen. In spite of the inherent errors of this approach, which may be significant, it must be recognized that, in many cases, oxygen values obtained 'by-difference' are adequate; for others, such as studies of coal weathering, more accurate values are required.

We have shown recently [2] that the nature of oxygen functional groups is important in assessing the degree of oxidation of a coal. In many cases it is impossible to know whether a particular coal has suffered oxidation purely from the 'by-difference' oxygen value because the overall oxygen content of the sample has not changed in a manner that is detectable by this approach.

Some years ago, a pyrolysis technique was developed for the direct determination of oxygen using the Perkin Elmer 240 Microanalyser [3]. This technique was based on earlier work, which showed that all of the *organic* oxygen in coal could be liberated by pyrolysis as $H_2O$, CO and $CO_2$. Culmo showed that the passage of the pyrolysis gases over hot activated carbon converts all the oxygen to CO. Subsequent passage of the CO over cupric oxide forms $CO_2$, which can be identified quantitatively by a suitable detector. The pyrolysis technique has been developed by other groups as well [4,5].

For a number of years, we have used this technique routinely in our work on coal oxidation where small changes in oxygen content are important [6,7]. However, although we have found this technique both useful and reliable, it does not provide information about the chemical *speciation* of

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oxygen in coal. This has led us to consider the use of thermogravimetry coupled to gas analysis by infrared spectroscopy (TG–FTIR) to measure organic oxygen in coal directly. Although this technique, developed by Solomon et al. [8], has been extensively used by our group [9–11] and others, it appears not to have been considered for this particular purpose. In this work, we report the application of TG–FTIR under pyrolysis conditions to measure total organic oxygen and examine oxygen speciation in the Argonne premium coal samples.

## 2. Experimental

The technique has been described elsewhere in some detail [9]. Here follows a brief description.

**TG–FTIR** — as mentioned above, the TG–FTIR technique has been developed and used extensively by Solomon et al. [8]. In the current configuration of the system, a Bomem TG/Plus TGA/FTIR spectrometer consisting of a DuPont 951 TGA, multipass gas cell, Michelson 110 FTIR and microcomputer was used. The system can simultaneously control furnace temperature, record weight loss and capture IR spectra for up to 20 evolving species in real time.

Typically, a 25–35 mg sample was continuously weighed in the TG/Plus system while heated using the following temperature program: a drying step at 150 °C followed by pyrolysis in helium with a temperature ramp from 150 to 900 °C at 30 °C/min. Gases and volatiles were entrained in a gas cell by a helium stream where the rate and amount of the IR-active species were quantitatively measured. During the thermal ramp program, infrared spectra are collected every 30 s. On-line analysis and post process manipulations of the data were performed by the TG/Plus and SpectraCalc software packages. In general, the spectra obtained from the coal samples showed absorption bands for tars, $CH_4$, $C_2H_4$, $NH_3$, CO, $CO_2$, COS, $SO_2$ and $H_2O$. The TG/Plus quantitative analysis program

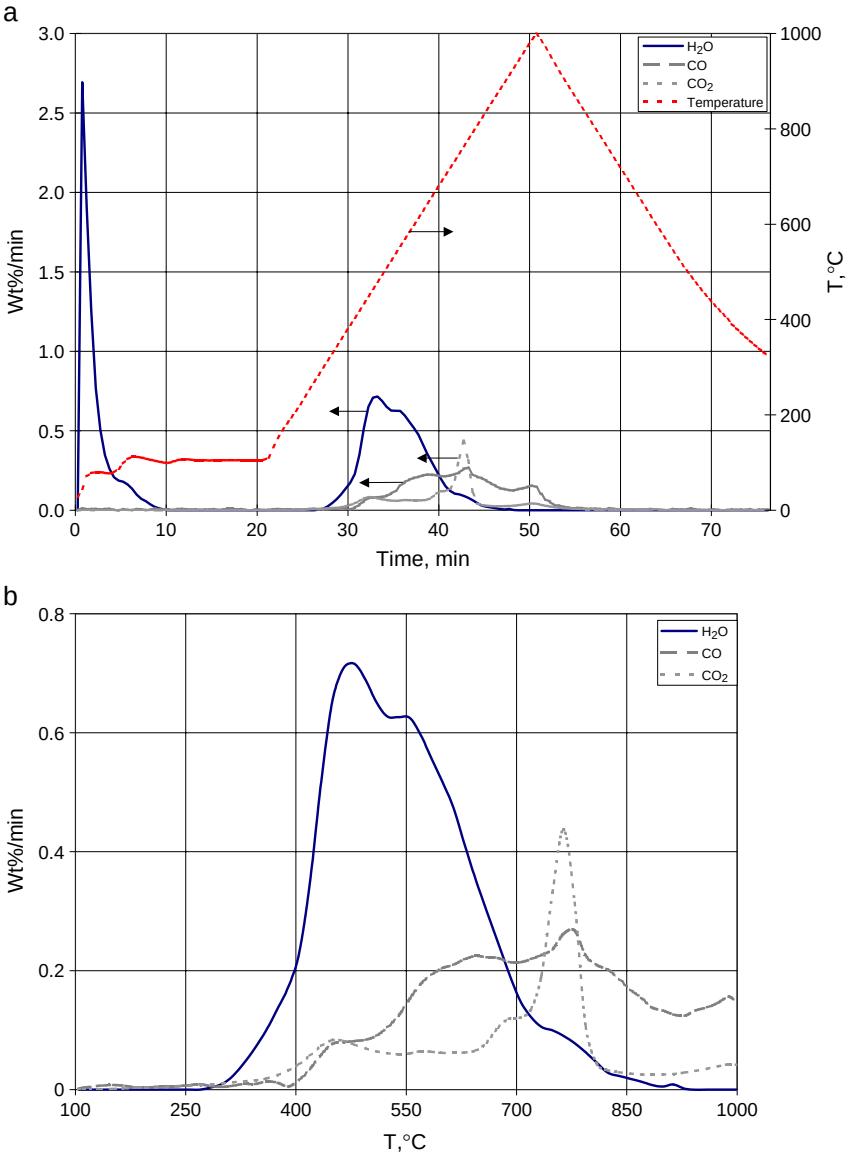


Fig. 1. Illinois #6 coal: (a) evolution of $H_2O$, CO, $CO_2$ and thermocouple temperature vs. time; (b) evolution of $H_2O$, CO and $CO_2$ vs. temperature.