

# Thermal analysis and coal assessment: an overview with new developments<sup>1</sup>

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## Abstract

Increasingly over the last 25 years, thermal analysis (TA) applications in the earth sciences have expanded rapidly, particularly for the assessment of coal, its constituents and products. A growing number of TA methods have been involved culminating in the use of thermomagnetometry (TM), high temperature DSC (to ~1500°C) and the wide ranging new method of proton magnetic resonance thermal analysis (PMRTA). In addition to the previously perfected and now widely utilized techniques of TA, “simultaneous thermal analysis” and “variable atmosphere thermal analysis” have proved invaluable particularly the latter where the furnace atmosphere conditions may be pre-selected, controlled and ultimately even changed repeatedly during individual TA runs. No longer is the characterization of the industrially valued properties of coal enough, varied and very useful as they have proved to be, but latterly TA is proving invaluable in the assessment of associated properties involving inorganic constituents and resultant fly or fluidized bed ash together with environmental implications for extraction, acid rain, disposal, recycling and alternate use. A range of contrasting applications is highlighted and the new PMRTA method and its applications discussed.

*Keywords:* TA; Coal; Proton magnetic resonance thermal analysis

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## 1. Introduction

Previously it has been indicated that the areas of advances in thermal analysis in relation to standards, refinement of existing methods, new methods and techniques, coupled methods and regularly published literature reviews have been responsible for the resurgence of applications in the earth sciences [1].

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Indicated elsewhere [2] were the main areas of application to thermal analysis to earth science materials. Of these the topics of material, identification, evaluation, reactivity, content of mixtures, industrial performance and quality control have continued to be particularly relevant.

Further, in relation to the application of these topics to fossil fuels, we must differentiate clearly between applications concerning the two fundamentally different components of coal, i.e. organic contents (coal macerals), wanted quality; and inorganic contents (mineral matter), unwanted, diluent/pollutants.

The organic components are those which come from the original plant material which was deposited in the peat swamp and eventually formed the economically important, hydrocarbon rich material coal.

From the examination of coal under the microscope (the science of coal petrology), a number of clearly recognizable constituents of indisputable plant origin may be identified (the coal macerals), e.g. those representing cellular structures, pollen grains, fungal remains and the much less structured material (vitrinite) which is essential for the formation of coke from coal on heating and of course bands, grains, infillings and veins of mineral matter [3].

The most important point to make here is that coal is a very heterogeneous material, the maceral and mineral components of which are difficult to separate out as concentrates for study.

It is these different constituent macerals composed of different hydrocarbons which constitute one of the main factors controlling the value and coking potential of coals. Another is the rank increase of coal from peat to anthracite, i.e. peat → brown coal → sub-bituminous coal → bituminous coal → anthracite.

A number of changes take place with increasing coal rank, i.e.

- hydrocarbon molecules become larger
- carbon content increases
- water content decreases
- volatile content decreases
- calorific value increases
- the quality and value increases

The coking potential of coal may be assessed by the microscopic determination of the macerals such as vitrinite which, during heating, froth up and become temporarily fluid before resolidifying again into a vesicular interstitial material binding the inert macerals such as fusinite together to form coke. Further, it is advantageous to determine reproducibly the degree of this fluidity and the temperature range over which it takes place as coal is heated up at a constant rate to beyond the temperature at which the coke making process is complete.

## **2. Thermal analysis**

Fluidity is determined by a standard method using an instrument called the Giesler Plastometer which represents a classical thermal analysis method but is surprisingly and erroneously not included as such in textbooks.

Briefly, it is composed of standardized charges of crushed coal placed in a cylindrical metal container around a vertically rotatable rod with lateral paddles to which a constant torque is applied. This container is then immersed in a solder bath the temperature of which is raised at a constant rate and as the coal becomes fluid the “stirrer” is able to rotate with firstly increasing and then decreasing velocity as the coal goes through its plastic range before solidifying again. Clearly the temperatures of the onset, maximum and end of plasticity plus the degree of fluidity may be measured in rotations per minute against increasing temperature.

In addition, the proximate analysis of coal is a fundamental, internationally recognised aspect of coal characterization involving the determination of four parameters, i.e. moisture, volatiles, fixed carbon and ash (derived from the inorganic mineral contents).

The determination of these by thermogravimetry (TG) [4] gives a good example of the new technique of “variable atmosphere thermal analysis”. It involves heating the coal sample on a thermobalance in flowing nitrogen to 110°C and holding it there isothermally to constant weight to give the weight loss due to water. The sample, still in flowing nitrogen, is then heated as rapidly as possible to 950°C and again held there to constant weight to give the loss due to volatile matter. At this point the furnace atmosphere is changed to flowing oxygen again to constant weight. A rapid weight loss occurs due to the burning away of the fixed carbon. The remaining weight is the amount of residual ash (see Figs. 1 and 2).

A further comparison of Figs. 1 and 2 clearly shows the difference in water, volatiles, fixed carbon contents, thus this method may also be used to assess the rank of coal [5] due to the variations in these, as listed above.

To date the ultimate application of variable atmosphere TG has been to municipal trash [6] where the amount of weight loss from cellulose can be distinguished from that from plastics (see Fig. 3). The widely ranging applications of TA to proximate analysis have been reviewed [7].

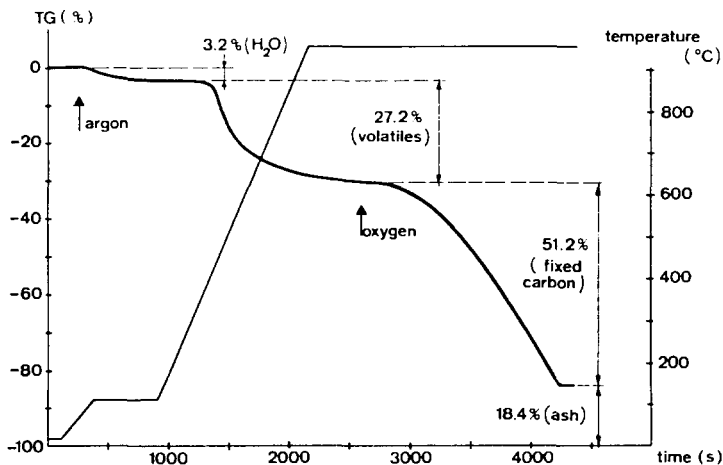


Fig. 1. Proximate analysis of a bituminous coal [5], re-published with the permission of Seteram.

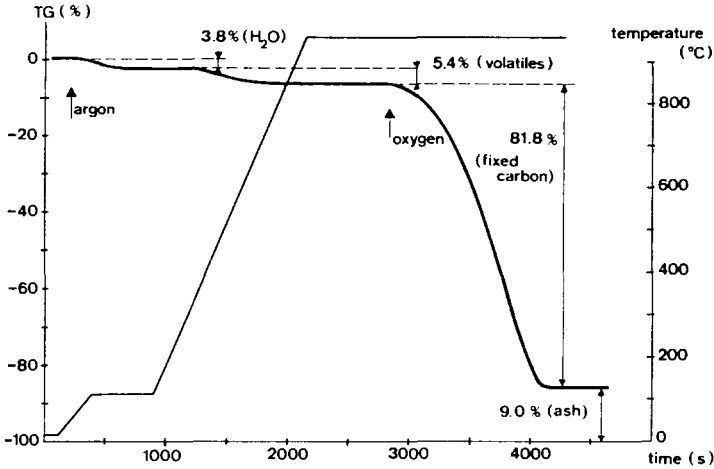


Fig. 2. Proximate analysis of an anthracite coal [5], re-published with the permission of Seteram.

In contrast are the inorganic/mineral components which almost entirely have been either:

- washed in (water)
- blown in (wind)
- transported in solution and precipitated
- altered after deposition

Those which are washed in as products of the erosion of the surrounding countryside as a function of climate and topographic relief require no further explanation.

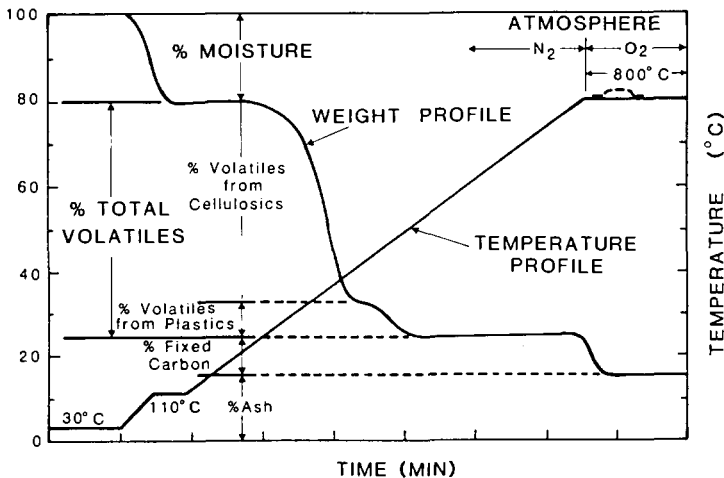


Fig. 3. The application of proximate analysis by TG to municipal solid waste/refuse derived fuels. After Agrawal [6], copyright ASTM, re-published with permission.

Contrary to first impressions the origins of the blown in materials are usually not from adjacent desert areas but result from the fine atmospheric particle fallout from explosive volcanic eruptions (ash). It must be further emphasized that the amounts of ash produced may be very large (several km<sup>3</sup> per eruption), and the areas of down wind deposition vary greatly, e.g. ranging from the 1980 eruption of Mount St. Helens spread across four US states to that of the Yellowstone eruption some 600 000 years ago which deposited ash on almost all of the United States of America.

It is clear therefore that the amounts and composition of the mineral matter washed or blown in are completely independent of the peat swamp environment, the conditions of which they do not reflect at all.

Mineral matter deposited in these ways usually occur in bands.

The converse holds true for the mineral matter which has been deposited from solution or has become altered after the peat has been laid down so that their deposition, amounts and composition are controlled by the conditions below the surface of the peat swamp.

Such minerals usually occur as replacements, relic cell infillings, individual crystals, pseudomorphs, nodules and veins or cleat infillings.

All the mineral matter (inorganics) irrespective of their origins; decrease the value of coal by: (1) acting to dilute the valuable organic contents; (2) individually or collectively being the cause of many negative aspects of coal utilization, e.g.

- ash or slag, physical characteristics
- washery rejects, acid run-off waters
- residue stability, chemical reactivity
- residue toxicity, heavy metal release
- residue disposal, land fill/reclamation (large amounts)
- acid rain, from burning coal

It is within this framework of economic factors that thermal analysis continues to produce valuable results in the considerable number of categories listed, as does the application of the new techniques of variable atmosphere thermal analysis” and “simultaneous thermal analysis”.

It is the areas of coal rank, coking potential, inorganic constituents, calorific values and environmental aspects which will now be considered further.

Previously it has been established [8] that by running in an inert atmosphere of flowing nitrogen or carbon dioxide the TA of the relatively few minerals which occur in any quantity in coals may often be altered quite markedly.

In addition TA has proved valuable as applied to minerals with respect to the following aspects:

- clear detection and identification
- most minerals decompose endothermically
- decompositions quantifiable by DSC/TG
- exceptions are those containing iron
- iron contents determinable by: (1) variable atmosphere thermal analysis; (2) thermomagnetometry

In the presence of oxygen the iron containing minerals which do not decompose endothermically are the iron carbonate siderite, and the iron sulphide pyrite. The presence

however, of the decomposition product iron may be detected at the end of a TA run in a completely inert gas if this is replaced immediately before cooling by air or oxygen where the oxidation of the iron gives a characteristic exothermic oxidation reaction or by thermomagnetometry [9]. The presence of mineral matter causes a reduction in the quality/value of the coal, in the following ways:

- dilution of the hydrocarbon portion
- interferes with combustion efficiency
- disposal cost of the residual ash
- ash, stability/reactivity
- ash, potential toxicity
- mineral compositions, ash fusion temperatures
- mineral endothermic reactions, reduce calorific value
- mineral compositions vary, calorific value loss.

To expand on these eight topics in relation to the mineral matter contents of coal:

- (1) It dilutes the wanted organic hydrocarbon portion of coal.
- (2) It interferes with combustion efficiency.
- (3) After utilization the inorganic ash remains and has to be disposed of in large quantities at significant cost.
- (4) The chemical stability must be determined.
- (5) This relates to the potential toxicity of this material and must be clearly established.
- (6) The mineral matter composition alters the ash fusion temperature to give a hot solid (good) or hot liquid residue (bad).
- (7) The dominantly endothermic decomposition reactions of minerals will clearly reduce the inherent calorific value of commercial coals.
- (8) Further, for a given gross mineral content of different coals their calorific values will be reduced by different amounts dependent on the types and proportions of the minerals present.

In the above list the first aspect may be assessed by DTA in air, by what are termed “combustion curves” [10] which also have the converse application of being able to detect small organic matter contents as impurities in mineral products and concentrates; or similarly by combined DTA/TG to give quantifiable results from the simultaneously determined weight losses [11]. The second, may be addressed by the use of high temperature DSC to measure the combustion characteristics of coals [12], together with the calorific value.

These aspects may also be investigated by identical simultaneous high temperature DSC/TG in flowing nitrogen of the as-mined coal (unwashed) and the upgraded beneficiated (washed) product of the same coal.

This will give a clear assessment of the degree of calorific upgrading which has resulted due to the different amounts of the mineral matter present which can be removed from coals from disparate seams and areas, particularly due to the grain sizes in which it is present.

Coal ash residues after utilization, may be investigated by simultaneous DTA/TG or variable atmosphere TG in different gas atmospheres such as flowing nitrogen, oxygen and carbon dioxide in order to determine particularly, residual carbon and reactive CaO contents [13]. Further, both reactions will show on DTA heating or cooling curves as

exothermic burning and re-carbonation reactions, the magnitude of which will be measured simultaneously or independently on the TG curve.

We are therefore now looking past the types of minerals present in coal to their proportions in relation to the calorific value distortions they may produce and the environmental implications the residual ash formed after coal combustion may have in the short and long term after disposal.

Having placed all this in perspective we turn now to a new method described recently, which embodies the determination of many of the parameters described in one innovative and simultaneous thermal analysis method, which is called proton magnetic resonance thermal analysis (PMRTA).

### 3. Proton magnetic resonance thermal analysis (PMRTA)

This new method, developed by the CSIRO Division of Energy Technology in Sydney, Australia is now commercially available. It is based on a bench top NMR unit linked to a computer as described in the literature [14] and was primarily developed for coal investigations.

A wide range of applications of PMRTA for the determination of economically important coal properties and indicating the complementary nature of this new method to DTA, DSC and TG are extensively covered in two papers [15,16]. However, it is clear that this

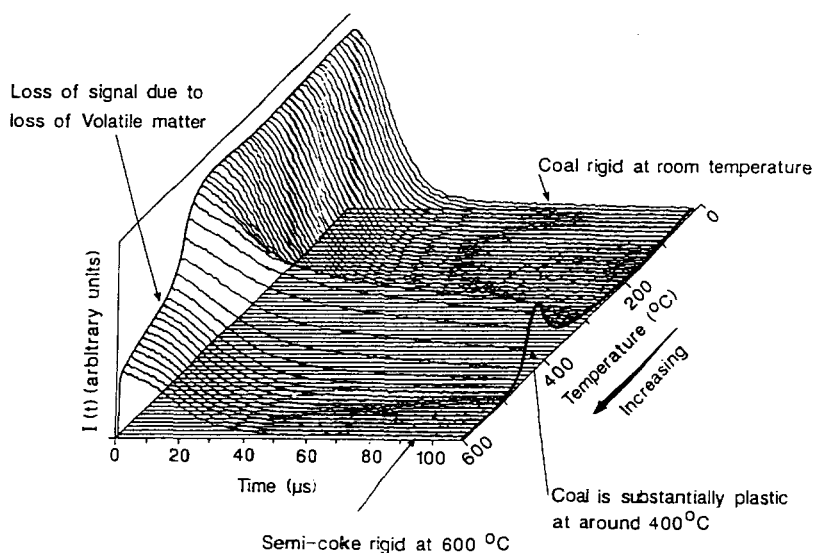


Fig. 4. Stacked plot of H NMR decay curve signals produced from a thermoplastic coal, plotted against time and temperature. From this can be obtained, as indicated, information on the temperature of plasticity, loss of volatile matter and return to the rigid state, viz. production of semi-coke. Reproduced with permission of CSIRO, Division of Coal and Energy Technology.

method also has wide ranging potential for applications to other hydrogen bearing materials.

The method uses signals from protons (hydrogen nuclei) in the coal sample under test, caused by their resonance on being excited by short bursts of radio frequency energy.

The resultant resonance quickly dies away for solids, but continues for much longer for fluids. With the coal sample being heated at a constant rate and with the resonance decay curves being determined every 1°C the PMRTA plot for one heating run coal from ambient to about 600°C is composed of a stacked array of NMR decay curves (see Fig. 4). Clearly this method can distinguish between fused or plastic material and the unfused or rigid material.

Looking carefully at Fig. 4 on its left hand side it may be seen that the degree of initial resonance with heating decreases as the coal gas volatile matter is driven off and the coal loses hydrogen. Further, at a low temperature there is an additional small loss due to a loss of hydrogen in the coal water content driven off.

When the termination of all these stacked decay curves is looked at against increasing temperature, on the right side of the diagram, a composite peaked trace can be clearly seen. For the coal in question (Fig. 4) this peak starts to rise at about 200°C which indicates the onset of coal plasticity. By about 380°C the coal has reached its maximum plasticity, while this peak has disappeared by about 520°C when the coal has become solid again. In this way, the onset, maximum and termination temperatures of plasticity, its plastic range, together with the peak height indicating the relative degree of maximum plasticity (or fluidity) may be determined.

In this way a number of parameters as determined by proximate analysis and Giesler plastometry may be determined simultaneously under exactly the same conditions from the same sample, including moisture and volatile contents.

Further, considering the measurement of evolved volatiles on heating by PMRTA, this will only show losses of hydrocarbon gases (containing hydrogen) so that for example losses due to the evolution of carbon dioxide from the decomposition of any carbonate minerals present in the coal will not be recorded.

As a result the volatiles as determined by the proximate analysis and PMRTA methods will separate the total volatiles from those of hydrocarbon composition, i.e. from the total of any others such as carbon dioxide or sulphur dioxide.

#### 4. Conclusions

Thermal analysis methods are playing a fundamental and increasingly valuable role in coal assessment in relation to both positive and negative parameters. It is envisaged that this trend will continue to expand with increased emphasis on the blending and mineral contents of coal, environmental aspects and the further development of new methods.

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