Journal of Thermal Analysis, Vol. 35 (1989) 219–242

Invited Review

APPLICATIONS OF DTA AND DSC TO COAL AND OIL SHALE EVALUATION

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(Received May 15, 1988)

With petroleum reserves limited, and nuclear sources increasingly unacceptable, the use of coal (and potentially oil shale) is rapidly increasing as is its content of inorganics (minerals). Thermal analysis techniques are particularly suited for the evaluation, characterisation, analysis, basic, applied and pollution research of such organic and inorganic fossil fuel materials. The type, composition, quality and thermal decomposition characteristics of which control the calorific value, volatile yield, petrochemical potential, coke and fly ash derivatives together with end product ash, slag and gases such as hydrocarbons, SO_x, NO_x and CO_2.

Within this context the specific contributions made by DTA and DSC are reviewed and the value/applications of this approach established.

I. Introduction

This review is designed to complement and update the thorough compilation of Lawson 1970, [1] and to highlight areas where expansion and advances have taken place since. Thus, for a comprehensive coverage, both should be read in conjunction with each other, bearing in mind that the present discussion covers both differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

The enormous increase in the wholesale price of oil, approximately 1600% between 1970 and 1981, arose from the predicted exhaustion of the world's plentiful resources of petroleum, the limited number of the sources of supply, the restricted nature of the means of transport and a dearth of oil self sufficiency in

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Akadémiai Kiadó, Budapest

most industrialised countries. This led to a search for alternative types and sources of energy and a marked upsurge in the use of coal for power generation, and renewed interest and vigorous investigation into methods of obtaining oil from coal and oil shale. An important part of this research has been played by the various methods of thermal analysis (TA).

Furthermore, with the trend towards the utilisation of progressively higher mineral content coals for electricity generation (up to 35–40% ash), [2] the emphasis in many cases has become directed towards a better understanding of the inorganic (mineral matter) contents. In addition, the amount of "waste material", either as mineral rich coal washery refuse (reject material) or power station ash, has to be catered for. Not only do very large amounts of this material require disposal, but as their impact on the environment must now be carefully considered, their organic and inorganic compositions must be studied to minimise heat generating reactions, spontaneous combustion, acid or alkaline mine dump leachate generation and to maximise their use for landfill reclamation, reafforestation, soil conditioning, and for fly ash as a neutralising agent interbedded with acid waste dump deposits and pozzolanic additives to light weight concretes.

The most comprehensive and recent coverages of the various applications of DTA to coals and oil shales, their organic and inorganic constituents, uses, together with waste and end products, occur as individual chapters in applied reference books or specialist reviews. These in turn contain excellent references to detailed and older works i.e. [1, 3–14]. Furthermore, the production of a set of temperature standards by the International Confederation for Thermal Analysis and the further studies [15, 16] have facilitated the calibration of DTA and DSC units on an international scale. In addition to the recognised TA abbreviations DTA, DSC, TG, DTG and EGA, others have been used here in i.e. PDSC (high pressure DSC), MS (mass spectroscopy), IR (infra-red), RF (radio frequency) and dielectric analysis (DA).

II. Applications

Most DTA research has been directed towards the higher rank "black" coals with lesser attention given to peat, brown coal and lignite. Also the determinations have more commonly been directed towards oxygen free furnace atmosphere conditions of N_2, Ar, CO_2 and vacuum.

The degree of purity and purging with these gases controls the efficiency, maintenance and balance of inert, oxidising and self generated furnace atmosphere conditions. These in turn considerably influence the resultant, often complex, DTA curves which have not shown sufficiently marked similarities, when determined from coals of different countries by different workers, for them to have been widely adopted as standard methods.

This extensive research on the dominant organic part of coal in relation to thermal decomposition, rank, individual petrographic constituents and carbonisation, which has received relatively little attention since the late 1970's has been thoroughly revieved [1], with some additions [5]. With the recent rapid advances in DTA, TG and DTG equipment, particularly in relation to plate thermocouples (free from direct sample contact attack), smaller and shallower sample holders and excellent atmosphere control, re-assessment of the above aspects is likely e.g. in relation to rank and shale content [17], rank [18] and organic matter contents [19]. This must be under strictly known and reproducible DTA conditions which also include sample size, thickness, grain size distribution, packing and gas type access and escape.

The valuable use of controlled preselected furnace atmosphere conditions i.e. "Variable Atmosphere DTA" has been developed and widely applied [9] while Warne [20] has been attributed with the introduction of this term [21]. More recently there has been renewed interest in studies with air available to the sample and the extension to include oil shales. Also the increasing use of large amounts of high ash coals has stimulated investigations of the inorganic (mineral) components in relation to detection, identification and rôle assessment, both negative and positive [2].

Furthermore, the complementary techniques of thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used individually to assist with quantification [22], thermal stability [23] and to provide "burning and volatile release profiles" [25][1]. The role of DSC and TG has been comprehensively reviewed by Rajeshwar [11, 12], and the technique of simultaneous DTA–TG–MS study of natural fuels described earlier [26] has been utilised e.g. [27–29], whilst simultaneous equipment has been utilised for DSC–GC and DSC–MS [30, 31] and for DTA–IR studies [32]. A current review of the literature indicates that DTA has a described, established and or potential rôle to play in a large number of areas of research, development, utilisation and economic assessment of solid hydrocarbon bearing fuels (see Table 1 below).

III. Coal

With the swing back to the use of large quantities of coal of all ranks,[2] increasing attention will be paid to its physical, chemical, combustion, organic and inorganic (mineral) characteristics, compositions and reactions. Furthermore,

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[1] Volatile release profiles have also been termed; "volatile release test" and "evaporation profiles" [24].

[2] In this series the coal rank is referred to as progressively increasing from peat, brown, bituminous coal to anthracite.

as the major uses of coal involve heating to produce changes and reaction, thermal analysis and particularly DTA/DSC techniques would appear eminently suitable for coal assessment, analysis and characterisation.

TABLE 1 Established. described and potential applications of DTA/DSC in the research development and economic assessment of solid hydrocarbon rich fossil fuels

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(1) Rank evaluation.
(2) Determination of ignition temperatures, including charcoals.
(3) Carbonaceous content assessment of (a) coal washery reject materials and (b) low quality mineral rich fossil fuel deposits.
(4) Fuel characterisation – as mined or after beneficiation.
(5) Residual carbon contents of process products, e.g. fly ash and spent shale.
(6) Carbonisation under various atmosphere conditions.
(7) Assessment of spontaneous combustion potential.
(8) Identification of specific minerals.
(9) Evaluation of mineral contents and variation trends.
(10) Production of mineral decomposition products including gases.
(11) Mineral thermal stability, decomposition temperatures and rates.
(12) Improved resolution and detection/identification of mineral peaks by variable atmosphere DTA.
(13) Improved detection limits of carbonate minerals in flowing CO_2.
(14) Mineral decomposition product reactions.
(15) Phase equilibria studies.
(16) The magnitude of endothermic/exothermic reactions involved.
(17) Isomorphous substitution in carbonate mineral groups.
(18) The detection of mineral crytallographic or phase changes including melting.
(19) Cooling curves to detect crystallographic reversions, phase changes and recarbonation reactions obscured by peak superposition on heating.
(20) Establishment and magnitude of the endothermic/exothermic nature of mineral and mineral component decompositions and/or reactions and their temperatures.
(21) Oil shale retorting conditions and practice; effects of heating rates, gas atmosphere type and heat balance.
(22) Fluidised bed reaction studies.
(23) The effects of catalysts on coal/oil shale temperature dependent processes, hydrogenation, liquefaction and retorting.
(24) Improved economic assessment of exploration, production, beneficiation and blended samples.
(25) The variations within and correlation of stratigraphic units.
(26) "Combustion curves" to portray the burning characteristics of coals.

A. Peat and brown coal

Peat and brown coal/lignite are characterised by high water contents (usually > 60% as mined), low calorific values and high contents of recognisable partially decomposed plant remains. Thermal analysis investigations of these low rank fuels are much less common than for "black coals" and to 1970, have been thoroughly reviewed [33].

The DTA curves of peats, determined in oxygen bearing atmospheres, are composed of marked exothermic effects, usually two peaked, in the 300–450° region which is preceded by a modest endothermic water loss peak at about 100°. Stewart et al. [34] concluded that the degree of humification, which increased with depth, was related to the intensity of the first exothermic peak. A further investigation using DTA complemented by DTG from four Spanish peat profiles, [35] confirmed the relationship of the first exothermic effect to depth, carbohydrate content and the inverse relationship to the content and nature of the humic acids present. In contrast, the displacement to lower temperatures of a) the two main endothermic peaks, and b) the first of these, has been directly related to the increased mineral contents and possible increased formation of organomineralic complexes respectively. In this context, the progressive fall in the temperatures of these two endothermic peaks may at least, in part, be due to the diluting effects of increasing contents of mineral matter, as established in a different context [36]. Further work [37] on peat and peat components has indicated the dependence of the second exothermic peak on contents of humic acids and cellulose.

In contrast, for lignites, [38] only slight modifications caused by bitumen and humic acids were found, while Rustchev and Stoyeva [39] investigated individual lignite lithotypes. Lignite curves are also usually characterised by two main exothermic peaks, although some from Japan exhibit only one [40, 41], and some brown coals three [42]. Heats of pyrolysis of a N. Dakota lignite in Ar, CO and H_2 have been determined using DSC [43].

The high pressure application of DTA to coal hydrogenation was initiated [44, 45] and studied in relation to catalysts [46]. It has been established that falls in the exothermic peak temperatures in response to the presence of various catalysts is associated with increased coal liquification/conversion e.g. [41, 47].

Rogers [42] compared DTA curves from lignite, brown, sub- bituminous and bituminous coals obtained under hydrogen (H_2) and nitrogen (N_2) at 8.0 MPa. In H_2 these, with the exception of the three peaked configuration of the brown coal, showed two large exothermic peaks at ~ 350–500°, the relative magnitude of which varied from one coal to another, with either one dominant or both ~ equal. By comparison the DTA curves of these coals determined in N_2 were rather featureless. Further investigations of one of these lignites, ion exchanged with Zn, Fe, Ni, Pb and Sn, always caused exothermic peak temperature reductions with this catalytic hydrogenation effect for Ni and Pb being even greater than Fe and Sn. Others have similarly investigated the catalytic action of additional materials [41, 45], while the effects of additions of alkaline carbonates to lignite chars [48] have been studied together with the results of inorganic compounds on the oxidation of an Australian brown coal [49].

B. Black coal

1. Coal determinations in air-oxygen

The DTA determinations of coal in air (or O_2) are essentially exothermic and their configurations, although influenced by compositional variations, both organic, inorganic and rank, represent the large amounts of heat generated by burning. The information obtainable under these conditions is relatable to combustion characteristics, ignition temperatures, and relative resultant heats of combustion. In the latter term, resultant is used because Warne [50] has shown that most common minerals in coal decompose endothermically within the combustion exotherm and will, to some extent, negate it. The large exothermic DTA effect recorded will thus be the resultant of these opposed reactions and will represent the calorific value (heat of combustion/heat content) of the material in question which is available for use and assessment [51].

The term "combustion curves" has been suggested [52] for the application of DTA to the monitoring of burning coal to distinguish it from the related DTG method, the curves from which are called "burning profiles" (a term initiated by Wagoner and Duzy, [53] and discussed in detail [25, 54]. The terms "volatile release profile", or "evaporation profile" have been used for the complementary DTG determinations in N_2 by Cumming [24, 54].

In general terms such DTA "combustion curves" of coal in air are composed of a very large, somewhat poorly defined exothermic feature located within the temperature range 250° to 900° (the maximum temperature is often lower), as described by several workers [1, 5, 50, 55, 56, 57]. Such combustion curves typically show two broad exothermic maxima, firstly due to the combustion of the volatile matter released on heating, followed by the burning of the residual fixed carbon. The additional initial small endothermic peak, due to water loss, may become quite large in the case of brown coals. The actual temperature maxima and range over which these burning phases take place, under standardised conditions, varies and is controlled by the effects of the coal variables mentioned above. Decreasing volatile matter yield, increasing rank and degree of graphitisation appear to cause increased peak temperatures. The vigorous nature of the burning reaction in air requires low sensitivity settings or sample dilution with Al_2O_3, and although flowing O_2 may be used to increase this peak intensity and detection limits of low organic matter samples [50], high organic content samples should not be run in O_2 as equipment melting may result [58].

Such DTA exothermic features located between 20–450° have been interpreted in terms of oxidation and internal burning, to be of predictive value in relation to spontaneous combustion for a range of Australian coals [59]. Weltner and Marinov [60] have attributed two peaks above 200° to the interaction of oxygen with nonaromatic and aromatic constituents in low and medium rank coals and note that only the latter peak is present for anthracite which has only an aromatic structure. In relation to this the curve obtained from an anthracite (6.9% volatile matter), just shows splitting to give two peak culminations [29]. The use of PDSC, [61] confirmed the double peak configuration between 150–450° for most coals, and that with increasing rank (lignite to anthracite), the relative size of the higher temperature peak area increased, whilst its area (attributed to aromatic content) and peak temperature are correlatable with fixed carbon content.

Marinov [62] has investigated the low temperature (20–300°) noncombustion oxidation of coals of different rank while the kinetic constants of coal decomposition in nitrogen have also been examined [63]. In contrast, the low temperature coal oxygen consumption and detailed "oxidation thermograms" to 600° have been related to structures [64, 65].

The first departure, extrapolated onset temperatures, point of sudden self-sustained temperature rise and peak temperatures of the exothermic "combustion curves", have been used to characterise the beginning of combustion (called ignition temperatures). This parameter has been determined for coals of different rank [66] illustrated for coal, coke and graphite, together with variations due to coke sample mass, [67–69] and a range of different charcoals [70]. These studies indicated ignition temperatures increased with coal rank and on to coke and graphite, but decreased with increasing carbon content of charcoals, to a high carbon content, where a sharp increase occurs. The effects on coal ignition temperatures of pelletising pressure and the rate constants of thermal decomposition have been described [71].

The vigorous DTA combustion exotherm of organic matter has been applied to the assessment of the heat content (calorific value) of coals, has been summarised [72] and quantified using DSC peak area measurements. Such determinations, in flowing O_2, have compared well with coals of known calorific value [73], ASTM Coals [74], and at elevated O_2 pressure (PDSC), with duplicate determinations using adiabatic calorimetry [75] compared to which, DSC provides details of the combustion reaction. Relevant to this is the discussion of problems of the burning properties of fuels as assessed by DSC and DTA [76]. Also, to confirm the existence of organic matter in sediments and soils [77], in fly ash related to defective power station coal combustion [5, 78], to characterise coke, electrode and reactor carbons [79] coal rank [18, 78], the degree of graphitisation of organic fragments (phytoclasts) in rocks of varying metamorphic grade [80, 81] and to various graphites and artificial carbons [78]. From a dilution sequence of coal with Al_2O_3, Warne [50] established the marked reduction in combustion curve size, together with a progressive fall in the second peak temperature, with decreasing coal content and a detection limit of at least 0.25%. Also suggested, were applications to the assessment of low quality high ash coal, oil shale, coal washery refuse and spent shale residues and conversely to low carbonaceous contents of powerstation ash, as inclusions in other rock and mineral materials, in fillers and for quality control.

2. *Coal determinations in non-oxidising conditions*

Due to the grossly exothermic overprinting effect of coal burning, other types of reactions taking place are not resolved on the resultant DTA curve. To nullify this effect, determinations have been made in furnace atmosphere conditions lacking oxygen. Thus N_2 (occasionally Ar, He or vacuum), CO_2 and self generated coal gas have been used to study the decomposition/pyrolysis reactions and kinetics of the coal organic (maceral) and inorganic (mineral) components collectively or individually, using vacuum, flowing gases and closed sample environments. Rajeshwar [12] has warned that the sensitivity of thermal behaviour to atmosphere type is extreme as even traces of O_2 can cause peak type reversals.

a. Coal determinations in nitrogen and carbon dioxide

The overall non-oxidative decomposition of coal and oil shale on heating has been shown to be endothermic initially, due to expulsion of water at low temperatures, followed by a modest (often poorly resolved), double reaction in the 400 to 700° region, due to the evolution of the hydro-carbon rich volatile matter, [22, 82] whilst additional endothermic peaks may be caused by the presence of minerals (see section IV below). Detailed investigations by others have recorded the presence of up to three endothermic peaks which have been related to gas evolution phases, cracking and coking processes e.g. [5, 73, 83] while the thermal stability of coke raw materials (also in N_2) [84] and the decomposition of graphite oxidation products [85] have also been studied.

Recent emphasis has been to identify the mineral caused peaks which are clearly recorded on the relatively featureless coal curves, produced in flowing N_2 gas, [6]. Furthermore, it has been found that the substitution of CO_2 for N_2 (flowing) produces similar "featureless" coal curves, but assists greatly in the detection and identification of carbonate minerals, [81], see section IV below.

Mahajan et al [86] and others [83, 87] have applied DSC to United States, Ohio and Kentucky coals respectively[3], while the DSC, specific heat determination method of O'Neil [88] was successfully applied to coals [89] and their pore network structure [90]). Hathi and Sliepcevich [91] have made a kinetic analysis of a variety of bituminous coals, while the thermal processes of coal pyrolysis have been investigated [92] and DSC applied to the hydrogenation of 20 US coals [93] and Earnest [94], using standard US coals, determined calorific values and by linked computerised data handling produced additional comparative information plots, against temperature, of the subtracted differences between pairs of curves.

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[3] used He gas at 5.6 MPa for pyrolysis studies of 12 US coals.

b. Coal determinations in other inert gases

On occasion, other inert gases (Ar and He) have been substituted with success for N_2. However, it is noteworthy that for valid content evaluations, allowance must be made for the smaller peaks which result from the same sample component contents when determined in gases of different thermal conductivity [95], i.e. Ar (and CO_2) and He have ~ 2/3 and 5.8 times that of N_2 respectively.

IV. Minerals in coal

The most comprehensive list of 87 minerals identified from coal has been compiled by Warne [2]. Most occur in minor amounts or under special conditions. Thus the minerals most commonly found in coal, listed alphabetically, as contents vary considerably between seams and locations, are as follows:

Calcite, Dolomite-Ankerite, Illite, Kaolinite, Montmorillonite, Pyrite/Marcasite,

Quartz, Siderite and Salt (in some brown coals)

As groups, clays are the most common, usually > 50% of the total mineral content, followed in decreasing abundance by silica, carbonates and sulphides. Thus the DTA of coal minerals has been restricted to those minerals which are present in amounts suitable for detection, identification and content evaluation by DTA. Several previous workers noted that coal DTA curves determined in an inert (combustion prohibiting) atmosphere resulted in relatively featureless curves, on which minor peaks might be attributable to the individual minerals present.

The definitive study of Warne [19] which followed, established that in inert conditions of flowing N_2, the DTA curve of coal was diagnostically modified by the presence of each of the minerals commonly found in coal. The detection limits established were in the order of 0.5% for pyrite and marcasite, 1% for calcite, magnesite, dolomite, and ankerite, 2% for siderite and kaolinite, 2 to 5% for quartz (depending on equipment sensitivity), 15% for montmorillonite and perhaps up to 30% for illite.

A linked, subsequent series of papers by the same worker, extended, clarified and applied this technique to the detection of the silica minerals [96], the resolution of kaolinite-siderite mixtures [97] and curve modifications with dilution for magnesite, calcite, siderite, and dolomite in various mixtures [36] and for siderite alone [98]. Also magnesium calcite [99] and minerals in lignites [100]. In addition, it was established, [81] that the substitution of flowing CO_2 for N_2 also effectively prohibited coal combustion, produced similarly relatively featureless coal DTA curves showing equally well recorded mineral peaks, in the same positions, with the exception of carbonates.

The effects on carbonates were quite spectacular. For the decomposition of carbonate minerals to take place the partial pressure of CO_2 gas surrounding the sample must be overcome. Thus, as this pressure increases, the carbonate decomposition reaction is delayed to take place at progressively higher temperatures and with an increased reaction rate [101]. The resultant single endothermic decomposition reaction peak of calcite ($CaCO_3$), siderite ($FeCO_3$), magnesite ($MgCO_3$) and rhodochrosite ($MnCO_3$), not only moves up scale to occur at a higher temperature, but becomes sharper [102] i.e. with the same area but decreased width and increased peak height. The result is an increased detection limit, a diagnostic peak movement (restricted to carbonates), and a method [103, 104] for resolving by preferential movement, carbonate peaks superimposed on peaks of other minerals which occur at similar temperatures in N_2 and remain unaffected by CO_2.

In contrast, the double and triple decomposition reaction carbonates, dolomite $CaMg(CO_3)_2$, and ankerite $Ca(MgFe)(CO_3)_2$, behave somewhat differently in flowing CO_2 compared to N_2. Thus in N_2 their diagnostic two and three peaked configurations progressively coalesce into a single peak as their content falls to about 10%. At this point their resultant single peak temperatures and that of calcite, although different, are sufficiently close to cause concern for their accurate identification. Conversely, in flowing CO_2 the two and three peaked configurations of dolomite and ankerite respectively are improved by increased peak separation, which is preserved right down to the limits of detection as the contents fall. Furthermore, the single peak of calcite moves considerably up scale, to a new higher temperature position, while the attenuation of all the carbonate peaks involved leads to increased detection limits [81].

As the Fe content of coal is detrimental in lowering the ash fusion point, its mineral occurrence is important in relation to removal by coal washing and preparation processes. The flowing CO_2 technique has been successfully applied to its detection in the form of siderite or amkerite [105]. Furthermore, the amount of Fe substituted in the isomorphous series dolomite-ferroan dolomite-ankerite, has been shown to be clearly assessable by this method [106], which is superior to others such as XRD. Thus, this CO_2 technique has been applied with marked success to the improved detection and identification of magnesite [102], siderite, calcite, dolomite and ankerite [81], siderite and ankerite, present together, [105], the increased detection limits of calcite and dolomite to ~ 0.25% [21] and the detection of magnesite when present with pyrite [107].

With one exception, no detectable inter-mineral or mineral decomposition product reaction appears to take place under these conditions to ~ 1000° [19] and confirmed [108], from a study of mineral fractions separated from American coals. Interaction is therefore not a complicating issue. The exception is that in the presence of pyrite the highest temperature peak of calcite, dolomite and ankerite, often suffers a considerable size reduction which is accompanied by a small exothermic fluctuation. The degree of peak size reduction increases with increasing pyrite content and appears due to the formation of Fe_2O_3, $CaCO_3$ [101].

A particular advantage of this method is that all the mineral matter present in a coal sample can be assessed, in its original state, without the problem of losses or alteration and contamination with coal which inevitably occurs to some extent by methods designed to separate a mineral concentrate from coal. An exception would be the temperature ~ 150° radio frequency oxygen plasma ashing (RF) method which has been perfected by [109] and quantified by [110] while the new glow discharge method [111] indicates a further advance.

Determinations in flowing N_2 of mineral rich organic matter poor bands (interbedded with coal) which show similar endothermic effects due to the decomposition of pyrite (at ~ 550°) and dehydroxilation of clays, may be resolved by a duplicate run in flowing O_2, where pyrite shows a large exothermic iron oxidation reaction, but the clays remain endothermic [94]. However, siderite decomposes endothermically at ~25° lower than pyrite [104] and in O_2 also has a vigorous exothermic oxidation reaction [98]. Thus it will also be confused with and separable from the clay mineral effects, but not in a diagnostically different way to pyrite. If present together, pyrite and siderite may be identified by an additional run in flowing CO_2, which, compared to the curve in N_2, will show the peak for pyrite unaffected but will move that of siderite up scale due to the increased partial pressure of CO_2 [104].

For the resolution and identification of other superimposed or overlapping mineral caused peaks, the "double differential thermal" technique [112] may be used. This involves adding to the reference what is considered to be an equal amount of one of the minerals, suspected present, in the unknown sample. Thus, peaks of this mineral (if it is the correct one, in the same amount) will be nullified and "disappear" from the resultant DTA curve. The mineral's presence is thus confirmed and the remaining peaks are left free from interference. This method is also useful for content evaluations in mineral mixtures as the amount added to cause complete nullification equals the amount in the unknown sample, [6].

Of the major carbonate decomposition oxides, only CaO will recarbonate on cooling in CO_2. Thus the "$CaCO_3$" component peak of calcite, dolomite and ankerite which may be obscured by superimposed peaks on the heating curve will show up clearly and alone as an exothermic reaction on the cooling curve. A size reduction of such a re-carbonation peak from a sample of known $CaCO_3$ content provides a measure of CaO used up on liberation to form calcium sulphate, thus reducing unwanted SO_x from stack emissions.

The whole topic of the evaluation by DTA of coal minerals has been reviewed in detail by Warne [6], and the role of variable atmosphere DTA in diagnostic mineralogy [20, 103].

The commercial development of high temperature DSC, its satisfactory calibration [16, 113] and the demonstration of its suitability for mineral studies [114], has led to its application to measuring the decomposition enthalpies of minerals in coal [115] and in detail for ankerites [116].

V. Coal residues

As the residues from coal beneficiation and utilisation processes remain after the removal of large amounts of organic material, they represent a marked concentration of the inorganic components and/or their reaction products. For this reason the detection of the mineral component peaks is enhanced, due to their larger size and the decreased to non-existant overprinting organic matter effects.

A. Coal washery wastes – Refuse

The study of the mineral rich coal washery reject materials by DTA has been neglected, presumably because this unwanted product, removed to upgrade coal quality, is considered "valueless". Pertinent, are the related studies of some coal dirt bands [117], coal mineral separated fractions, [108] gangues from coal mines [118] and the assessment of residual carbon [50].

Such waste is suitable for detailed attention as tens of millions of tons produced per annum must be dumped, used for land reclamation, as a construction aggregate, a source of clay minerals or metals recovery, as a horticultural soilless media [119] or for a low quality fuel. In all cases its mineral content, forms, stability, potential for reaction, weathering susceptibility, pollution and further utilisation cannot continue to be ignored. It is noteworthy that the mineral contents of washery wastes cannot be assumed to be the same as the individual coals from which they are derived. Thus, the coarser and more freely liberated mineral fragments will be more easily separated, whereas the finer fragments remaining in the coal may not be of the same type or composition nor may their size distribution be uniform.

B. Coal ashes

Differential thermal analysis is applicable to four types of coal ashes produced by radio frequency (RF) oxygen plasma at ~ 150°, low temperature (370–400°), high temperature (815°) oxidation and residues of power station combustion (including fly ash), which respectively produce accumulations ranging from unaltered mineral components to their glassy and recrystallised resultants. The increasing production and use of large quantities of powerstation ash indicates an urgent need for detailed knowledge of its compositions and properties. Such research has already been initiated [120].

Applications of DTA are for mineral identification and content evaluation, the detection of residual phases, including carbon and water absorption (as under IV above), melting point-ash fusion determinations, new phase formations[4] and equilibria studies (up to 1500°), together with hardening, hydrolic, pozzolanic and soil conditioning properties. These aspects have been thoroughly reviewed [5] and require no further comment. Recent additions are the studies of fly ash, chlorination with bauxite, in the presence of carbon to estimate the reactivity of Al [122] and volatility to 1400° using coupled DTA/TG/MS to identify and quantify species evolved with regard to melting point and possible toxic releases during industrial uses involving re-heating [123].

Subsequent DTA in air of RF oxidation residues has given detailed oxidative profiles for various amounts of pyrite (FeS_2) alone and its recognition in RF ash [124] has been extended by Earnest et al. [125] to detect other common coal minerals, including the conflicting effects of the concurrent presence of pyrite and szomolnokite ($FeSO_4.H_2O$) and the possible presence of rosenite ($FeSO_4.4H_2O$), melanterite ($FeSO_4.7H_2O$) and coquimbite ($Fe_2(SO_4)_3.9H_2O$) [94].

Applications to RF ash of the coupled DTA-system, using non- dispersive IR gas detectors, described by Morgan [32] holds much promise. It monitors the evolved gases, H_2O, CO_2, CO and SO_2 down to contents of 100's of ppm to identify minerals in small amounts which give off these gases at specific temperatures i.e. individually or in mixtures [32], the common anhydrous carbonates [126], members of the dolomite-ferroan dolomite-ankerite series [127] and pyrite [128].

C. Coal liquifaction residues

The mineralogy of coal liquifaction residues has been tabulated by Alpert and Wolk [129], while Shibaoka and Russell [130] have investigated batch autoclave residues, and Earnest [131] has included DSC in his review on the characterisation of coal liquifaction residues. Conversely Yokoyama et al [165] have investigated the catalytic activity of various iron sulphides in coal liquifaction. In general, DTA and DSC have a valuable rôle to play in the characterisation of these residual or newly formed inorganic compounds resulting from coal liquifaction processes, particularly where their reduced crystallinity may not give adequate identification by other methods.

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[4] For a comprehensive list of 33 phases recorded by several methods, see [121].

VI. Oil shales

The ~1600% oil price rise between 1970–81 and its predicted decline in production by year 2000 have focused attention on the previously uneconomic, but vast deposits available of oil shale (and oil/tar sands), as an alternative source of "petroleum" products. Extraction is by various methods of retorting, which will involve heating the parent oil shale. Thus TA methods are most suitable, have been increasingly applied and offer great scope for determinations of quality, hydrocarbon yield, effects of catalysts, mineralogy, decomposition, heat balance mechanisms and kinetics together with residual product reaction identifications, spent shale composition/stability, low grade fuel potential and specific and potential further utilisations.

The early work e.g. [132, 133] has been followed by a strong renewal of interest generated by the 1970–81 "oil crisis". Because of the detailed heat balance variations of raw products and different retorting practices, DSC and PDSC have been favoured over DTA, and complemented by other TA methods, particularly TG and DTG, Rajeshwar [11, 12], who also documented the use of DSC for specific heat determinations. The applications of DSC to the characterisation of oil shales has been summarised [134], and the whole subject of "Oil shale analysis methods", including TA, reviwed by Williams [13].

Thermal effects have been shown to be extremely sensitive to variations in atmosphere composition [10, 135, 136], which should be known and reproducible, while the dependence of exothermic features on a number of experimental conditions, has been described [92]. Investigations by DTA and DSC have provided a wide range of information about oil shales/tar sands from a number of countries e.g. from Australia, Canada, Colorado (USA), Egypt, Israel, Jordan, Tasmania (Australia) and New Zealand, whilst the major world deposits are listed [10].

A. Oil shale determinations in air-oxygen

When heated in readily available, often flowing air or O_2, oil shales undergo rapid combustion which typically shows as a large composite, multiterminated exothermic feature, similar to the DTA "combustion curves" or DTG "burning profiles", (see under section B1 above). The kinetics of such DTA curves obtained from the combustion of oil shale and char have been compared [137].

Typical of these are those of Rogers and Bibby [52]. To illustrate heterogeneity DSC has been applied [138], to measure combustion enthalpies for Green River [139] and New Zealand [52] oil shales, pyrolysis enthalpy and thermal stability of Athabasca and Utah oil sands [140, 141] while the latter determinations are in agreement with those from Athabasca oil sands alone as determined with PDSC

[142]. These thermal effects are weak, but may be enhanced from bitumen extracts [141].

B. Oil shale determinations in inert gases

In this category CO_2 has been included as it similarly prohibits combustion. In an inert atmosphere the DTA of low mineral content oil shales show as a moderate endothermic feature at ~500° dependent on source, type and rank [22, 143, 144] while Rajeshwar et al [143] have developed the simultaneous application of DTA and dielectric analysis (DA). The DTA kinetics of oil shales from Jordan (in He) have been determined [145], while the decomposition kinetics of British Kimmeridge oil shales have been determined using DSC [146].

Using DSC, a linear correlation between the enthalpy of decomposition (area of pyrolysis endotherm) and oil yields were established for Green River oil shales [134]. Phillips et al. [142] studied Athabasca oil sands using PDSC, while high pressure DTA was separately used to evaluate separately the catalytic effects of zinc and tin (11) chlorides on the hydrogenation of Tasmanian alginite under nitrogen and hydrogen [46]. Also DSC has been used to characterise Australian oil shales [147], to study chemical and structural transformations in Green River oil shales [148], to compare thermal characteristics of U. S. Devonian and Green River oil shales [149] and low temperature oil shale conversion [150].

VII. Minerals in oil shale

From the Green River formation a large number of minerals, some in ore grade amounts have been described.[5] The DTA characteristics of minerals commonly present have been (a) illustrated from a complex mixture curve [3], (b) reviewed for a wide range of carbonates, together with clays, zeolites and sulphides [151] and specifically for gaylussite [152], (c) related to the increased enthalpy due to analcime [135], (d) tabulated from a number of previous sources [10] and (e) characterised from comparative sets of curves of individual minerals determined separately and in mixtures with oil shale [22]. However, with the increasing number of different oil shale deposits described, it appears that much simpler mineralogy (similar to coal) and illustrated individually [153] and perhaps typified by the Australian deposits, is much more common [22, 103, 154].

Detailed mineralogical aspects are vital to oil (and spent) shale characterisation, evaluation and utilisation, because of its high mineral content (usually >50%) and the heating of this whole rock or its only moderately

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[5] Namely 70 authigenic minerals including many cabonates [166]

mineralogically lower beneficiated product. For this, individual mineral thermal effects must be recognised, their thermal behaviour established, particularly in relation to any possible mineral component interaction, catalytic dilution and different gas atmosphere effects. For example, in the latter case, siderite ($FeCO_3$) in N_2 decomposes with a single large endothermic reaction to give FeO and CO_2, but in the presence of O_2 the FeO produced immediately oxidises exothermically so strongly that the net product of these reactions is a small exothermic resultant compared to a large endothermic reaction in N_2 [98].

As with coal [50] it is necessary to prohibit, using an inert atmosphere, the massive exothermic burning effect of oil shale in order to record the smaller endothermic peaks of the individual mineral contents present. With this technique, using flowing N_2 or CO_2, a series of complementary papers have provided detailed information. Initially the relatively featureless DTA curve of a low mineral matter content oil shale decomposition (pyrolysis) indicated [3] was confirmed and shown [22] to be composed of two broad endothermic features. Firstly, from ambient to 150 to 200°, due to the release of absorbed and clay associated water, secondly (for low rank material) by one peaking at ~450°, which is due to the evolution of gaseous hydrocarbon contents, the actual endotherm of which will vary up scale with increasing rank.

Two noteworthy points were made [22].

1. That the initial water evolution endotherm will also contain water released from any hydrated sulphates present and in particular that of gypsum will show as an additional narrow sharp peak on the high temperature side (at ~130°), and
2. That the "450°" hydrocarbon volatile matter release peak must also represent the evolution of valueless and even deleterious non-hydrocarbon components, (H_2O, CO_2 and SO_x) which are liberated from the minerals present which decompose at this temperature. The presence of such endothermic decomposition reactions, not only robs heat from the retorting process, but adds dilutants to the hydrocarbon gas yield. This results in a decrease in calorific value and an increase in removal costs.

The detailed work on the effects of adding 20% of individual minerals to a low mineral content oil shale [22] has shown that the clays, illite and kaolinite, the carbonates siderite and magnesite and the sulphides pyrite and marcasite also decompose in the 350–550° oil shale volatile evolution zone to yield H_2O, CO_2 and SO_x. Conversely the gaseous yields from the minerals montmorillonite, dolomite, ankerite and calcite are not produced until progressively higher temperatures are reached i.e. after the hydrocarbon volatile matter yield is completed.

The same authors have shown that greatly improved detection limits, peak resolution and separation and therefore identification of the carbonate minerals, siderite, magnesite, dolomite and ankerite, occur in atmospheres of flowing CO_2 compared to N_2. Furthermore, by preferential up scale movements of the single peak of siderite and/or magnesite, the presence of these two minerals may be confirmed. This is particularly important when in mixtures with pyrite, as their peak positions in N_2 are closely adjacent on either side[6] to that of pyrite, whose position remains the same in N_2 and CO_2 [104].

In CO_2 the peak of calcite, also moves up scale and attenuates [21]. However, with Rundle (Australia) oil shale this peak movement is further and occurs with a much reduced size [155], who additionally could not substantiate by XRD or microprobe analysis that this was due to the formation of wollastonite ($CaSiO_3$). An alternative explanation put forward involved the formation of portlandite ($CaOH_2$) which was identified and the decomposition of residual calcite. This phenomenon is important as the non-recognition of this drastic peak size reduction would result in poorer detection limits, spuriously low content evaluations and lack of detection of significant contents due to the unexpectedly small or non-existant calcite peak and its anomalously high temperature position.

Pertinent to this are several kinetic studies i.e. in relation to calcite plus dolomite in the Colorado and on calcite alone in the Julia Creek (Australia) oil shales. These studies gave comparable activation energies, although the decomposition rates were ~6 times faster for the US material. It was also found that such calcite decomposition reactions were much less endothermic than calculated for the simple calcite decomposition reaction alone [157]. This was explained by the inclusion of the wollastonite formation reaction, the kinetics of which were subsequently determined in the temperature range 750–960°, (from samples preburnt in air to remove the organics) in relation to the effects, on possible formation rates, of a number of variables [158].

In flowing CO_2 the characteristic two and three peaked configuration of dolomite and ankerite is preserved right down to the limits of detection, without the peak fusion at low contents which occurs in N_2 [21, 105]. Furthermore, the amount of Fe substituted in the dolomite-ferroan dolomite-ankerite series is directly relatable to the size of the middle peak and clearly distinguishable in mixtures with siderite [106].

In energy determinations and organic content evaluations [12, 50] it has been pointed out that the thermal effects of the mineral contents are often considerable and neglected, although a good example of effects of dawsonite, nahcolite and nordstrandite, has been given [144].

VIII. Oil shale retort residues

Because of the high, close packed fine grained mineral contents, and considerable residence times at elevated temperatures during retorting, oil shale, mineral and mineral product reactions may be expected. Thus, the retort spent

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[6] May even be somewhat superimposed due to crystallinity differences.

shale chemical/mineralogical compositions are important for their possible use as (a) low quality fuels [50], (b) ceramic and light weight aggregate materials [159] and (c) land fill/afforestation and soil conditioners i.e. physical, weathering speed, and acid, alkali or heavy metal leaching potential, and the environmental implications of such factors regarding re-use, disposal or rehabilitation of this material in vast quantities.

Dependent on the original mineralogy and the marked effects of different gas atmospheres [156] a number of possible different reactions should produce a range of new components. Calcium and magnesium silicates [156, 158] should be common (for high retorting temperatures) and stable, whilst low silica high carbonate contents would produce excess MgO and CaO [155] in the spent shale product. However, Mg and Ca carbonates and oxides will combine with SO_x (released from pyrite) to form sulphates [160] which in turn are subject to bacterial attack on disposal to release sulphuric acid. Alternatively, in readily available CO_2 any CaO liberated from carbonates rapidly re-carbonates which shows clearly as an exothermic reaction on DTA cooling curves [161]. Furthermore, only CaO recarbonates whilst any Mg, Fe, Mn, Zn or Pb oxides from the decomposition of other carbonates e.g. magnesite, siderite, dolomite or ankerite will not [9]. This is supported by a cyclic calcination-recarbonation study [162].

The effect of higher oxidation temperatures of residual carbon associated with dolomite compared to magnesite was investigated [163]. Although considerable TG research has been undertaken in this area (see 4 papers in Thermochim. Acta, V. 26), the established potential of DTA, as applied to coal ashes, has not been utilised, although many directly applicable aspects have been described above in other contexts.

IX. Conclusion

The swing back to power generation from coal, the renewed interest in oil from coal and oil shale and the increasingly important rôle of mineral contents have resulted in a marked expansion of research. As the major uses involve heating, TA methods, particularly DTA (and DSC), sometimes coupled with EGA methods, are well suited for the characterisation, evaluation, assessment and analysis of a large number of coal and oil shale properties (Table 1), some of which are in wide routine use.

Reproducible variable atmosphere conditions facilitate or prohibit various reactions and determinations e.g. combustion curves and pyrolysis reactions respectively. Furthermore, compared to N_2 mineral DTA in flowing CO_2 increases the detection limits of carbonates, their identification by preferential up scale movements and peak separation and alleviates problems of peak superposition. In addition for low temperature RF ash samples, the marked exothermic oxidation peaks of pyrite and siderite produced in O_2 (but absent in N_2) clearly indicate their presence which is usually masked by kaolinite.

The thermal reactions undergone by minerals are important to the overall heat yield/balance and catalytic effects, particularly in relation to oil shale retorting, while the composition and stability of the resultant residues (e.g. powerstation and spent shale ashes) are of increasing importance to their use or disposal. These methods are equally applicable to the organic and inorganic components, often simultaneously, and may be used under preset heating rate and atmosphere conditions, are amenable to automation and routine use to provide a wide variety of information of both fundamental and technological application. Furthermore, much information of general and potential application is to be found in the two volumes of "Differential thermal analysis" edited by R. C. Mackenzie [164].

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The authors are indebted to Mr. D. B. Warne for his extensive and meticulous assistance with literature searches and topic cross referencing.

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For future reviews S. St. J. W. would appreciate receiving reprints from authors of papers over the whole field of the thermal analysis of Fossil Fuels.

Zusammenfassung — Wegen der begrenzten Ölvorkommen und der wachsenden Unakzeptabilität nuklearer Energiequellen kommt es zu einem schnellen Anstieg des Verbrauches an Kohle (vor allem an Ölschiefer). Dies gilt auch für deren Gehalt an anorganischen Stoffen (Mineralien). Zur Auswertung, Charakterisierung, Analyse, Grundlagen-, angewandten und Verunreinigungsforschung solcher organischer und anorganischer fossilen Brennmaterialien sind thermische Untersuchungsmethoden besonders geeignet. Art, Zusammensetzung, Qualität und Charakteristika der thermischen Zersetzung bestimmen den Kaloriewert, den Flüchtigkeitsgehalt, das petrochemische Potential, den Anteil an Koks-, Flug- und Endproduktasche, Schlacke und Gasen wie z. B. SO_x, NO_x und CO_2. In dieser Mitteilung wird ein überblick über die einzelnen DTA und DSC Untersuchungen gegeben und über den Wert und die Anwendbarkeit dessen berichtet.

Резюме — В связи с ограниченным запасом нефтяных источников и все более усиливающейся тенденцией против использования ядерных сточников, быстро увеличивается использование угля (и потенциально горючих сланцев), также как и содержащих его неорганических минералов. Методы термического анализа особенно примеными для оценки, характеристики, анализа, фундаментальных, прикладных и экологических исследований таких органических и неорганических материалов. Термические методы позволяют определять тип, состав, качество и термические характеристики разложения, теплотворную способность, выход летучих продуктов, нефтехимический потенциал таких материалов, образование кокса и летучей золы, наряду с такими конечными продуктами разложения, как зола, шлак и газообразные углеводороды, SO_x, NO_x и CO_2. В рамках такого контекста приведено обозрение методов ДТА и ДСК и приведены оценки использования такого подхода.