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# Thermal analysis—a resurgence in the earth sciences: with applied, industrial and environmental aspects [a]

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## Abstract

Applications of thermal analysis methods are expanding rapidly in the earth sciences and range from specific minerals, mineral mixtures, members of isomorphous substitution series, ceramics, cements and natural materials characterization, industrial evaluation, performance, thermal stability and quality control, proximate analysis, inorganic contents and calorific values of solid fossil fuels to the assessment of environmental aspects of mineral residues, fly ash and the release of $SO_2$ and its extraction from evolved (and flue) gases by various sorbents together with their regenerative capacities. Of particular importance is the application of the new generation of methods such as derivative thermogravimetry, evolved gas analysis and thermomagnetometry, together with utilization of the techniques of simultaneous thermal analysis and variable atmosphere thermal analysis.

## INTRODUCTION

Over the years, attention has been drawn to many invaluable accounts of the first or very early examples of thermal analysis (TA) in general or in specific areas in particular. These studies have been incorporated by Robert Mackenzie in his fascinating work “A History of Thermal Analysis” [1]. However, there seems little doubt that the series of scientific investigations published by Henry Louis Le Chatelier, which culminated in 1887 in the development of his ingenious automated differential thermal analysis (DTA) unit and its application to minerals [2,3], laid the foundations for the applications of thermal analysis to mineralogy and the earth sciences. His innovative equipment, utilizing his refined platinum/platinum–rhodium thermocouple, warrants a brief description. It consisted of a delicate mirror galvanometer connected to a thermocouple in a powdered clay sample. The sample was then heated uniformly at 100 °C $\min^{-1}$ while the mirror of the galvanometer reflected onto a photographic plate the flashes from an induction coil which sparked every 2 s.

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APPLICATION AREAS OF THERMAL ANALYSIS
EXAMPLES IN THE EARTH SCIENCES

MINERALS
MINERAL MIXTURES
ISOMORPHOUS SUBSTITUTION SERIES
SOILS
CERAMICS - CEMENTS
CONCRETE AGGREGATES
BUILDING STONES
INDUSTRIAL RAW AND END PRODUCT MATERIALS
FOSSIL FUELS
WASTES-MINE, COAL WASHERY, ASH, GASES
ENVIRONMENTAL ASPECTS

Exhibit 1.

Thus, on the developed film, lines representing the sparks appeared equally spaced when the sample temperature increased at the same rate as the furnace, but were closer together if the sample temperature increased more slowly during an endothermic reaction, or were more widely spaced if the temperature increased more rapidly due to an exothermic reaction. Temperature calibration was achieved from the boiling points of water, sulphur and selenium, together with the melting points of gold, determined under the same conditions.

The rapid and somewhat chaotic expansion of mineralogical applications was brought to order in the several publications by Robert Mackenzie [4–6] which included the "Scifax Differential Thermal Analysis Data Index" and culminated in the two ageless companion volumes entitled "Differential Thermal Analysis". These were complemented by the publication by Schultz [7] and the comprehensive re-appraisal, using the same DTA unit, coupled with the introduction of the concept of "Proben-Abhangigkeit" (PA) curves (i.e. curves of sample-amount dependence) by Smykatz-Kloss [8]. These works of consolidation, compilation, review and new contributions have been ably carried forward by such recognized earth scientists as Todor [9], Garn [10], Wendlandt [11], Dollimore [12], Morgan and coworkers [13–15], Rajeshwar et al. [16], Warne and Gallagher [17], Earnest [18,19], Rustschev [20], Heide [21] and Warne and coworkers [15,17,22–25]. The current resurgence in the application of thermal analysis to the earth sciences covers an extensive range of topics, examples of which are given in Exhibit 1.

## METHODOLOGICAL TRENDS

For a very considerable period of time the emphasis was almost entirely on the applications of DTA, which resulted in the publication of some major contributions [4–8]. This method was subsequently complemented by thermogravimetry (TG) to give improved quantification of the thermal reactions recorded. At this point, due perhaps to over-claiming the merits of TA and its being overshadowed by newly developed methods which ranged from infra-red and atomic absorption spectroscopy to X-ray fluorescence and the electron microprobe, the use of TA in the earth sciences settled into a period of "the doldrums".

However, the simultaneous development of new TA methods and techniques over the last 10–20 years, coupled with the availability of reference materials and regular TA literature reviews by Murphy, followed by Wendlandt [26] has led to a resurgence in the use and value of a wide range of TA applications in many areas of earth science.

Herein a distinction is made between new methods and new techniques. The former refer to the measurement of specific new temperature-dependent parameters, i.e. magnetism (thermomagnetometry (TM)) or sound (thermosonimetry (TS)), while the latter cover the utilization of existing methods in a different way, i.e. by the application of "variable atmosphere thermal analysis" or "simultaneous thermal analysis".

## *New methods*

The new methods which have proved particularly valuable are, in approximate order of importance and with a good reference for each: evolved gas analysis (EGA) [27], derivative thermogravimetry (DTG) [28], high temperature (to about 1500°C) differential scanning calorimetry (DSC) [29], TM [30] and thermomechanical analysis (TMA) [18]. An excellent description of these and other new methods has recently been published by Brown [31].

## *New techniques*

As new techniques are applied to already established methods, they will be considered in detail as they show, to advantage, the often complex applications involved. The role of the new techniques has been to greatly extend the value of existing methods. For example, the simultaneous application of more than one TA method to measure several parameters from the same sample under identical conditions forms the basis of "simultaneous thermal analysis". In contrast is the concept of "variable atmosphere thermal analysis" where the furnace atmosphere conditions may be preselected, controlled and even changed during TA runs.

### *Simultaneous thermal analysis*

The results from simultaneous TA determinations provide much valuable information. Coupled DTA/TG gives quantification of mass variations representing DTA peaks [32], DTA/EGA or TG/EGA [33] identifies the gaseous products released from specific reactions (see Fig. 1). This has

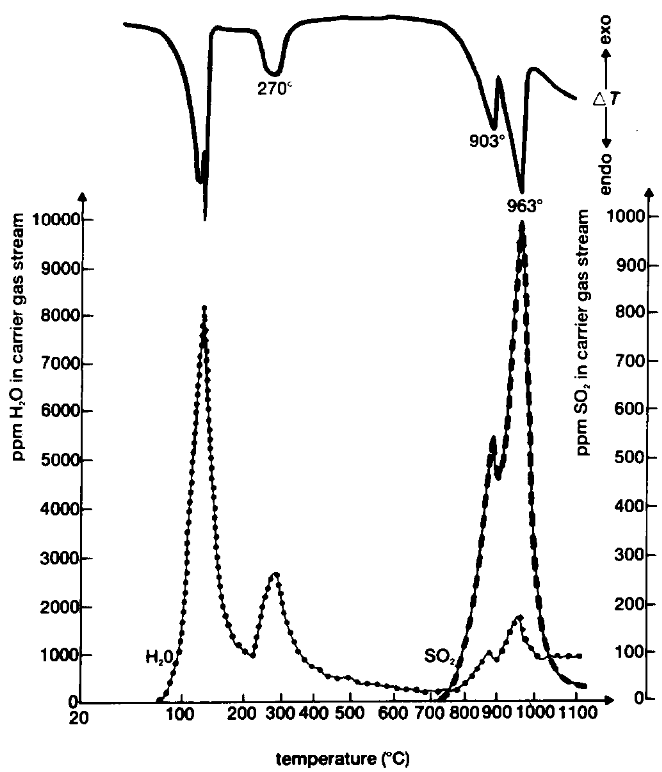

Fig. 1. Simultaneous DTA–EGA curves of $CuSO_4 \cdot 5H_2O$ using non-dispersive infra-red analysis for determining $H_2O$ and $SO_2$ evolution during heating. (After Morgan [13] with permission.)

applications in mixture component identification, specific pollutant gas recognition and their release, entrapment and recombination temperatures.

The addition of DTG to TG or other techniques such as DTA provides further definition and resolution of closely spaced reactions which appear superimposed on TA curves [14,33]. Simultaneous TM/DTA allows for the linking of magnetic phases to DTA peaks or with the evolution of specific gases if TM/EGA is used. Furthermore, if DTA/TG/DTG/EGA are done simultaneously, close mass changes can be resolved, related to reactions on the DTA curves and to associated gas evolution peaks to give invaluable compositional and decompositional information. Finally, added definition, sensitivity and calorific value data may be obtained by substituting differential scanning calorimetry (DSC) for DTA.

### *Variable atmosphere thermal analysis*

Here the controlled furnace atmosphere conditions may be preselected, i.e. static or flowing, maintained or changed as desired between [34] or during runs, with preset combinations of different purge gases used sequentially [35], and as gas mixtures [36] or, conversely, vacuum, using dynamic,

VARIABLE ATMOSPHERE THERMAL ANALYSIS CONDITIONS

PRE-SELECTED GAS
VACUUM
STATIC
FLOWING
MAINTAINED
CHANGED
(BETWEEN OR DURING RUNS)
COMBINATION OF GASES
(SEQUENTIALLY OR AS MIXTURES)

Exhibit 2.

isothermal [35] or quasi-isothermal heating rates [37] (see Exhibit 2). This technique may be equally well applied to single or simultaneous methods.

## EARTH SCIENCE APPLICATIONS

### *Materials in the earth sciences*

In general terms, TA may be applied to earth science materials in a number of ways, examples of which are set out in Exhibit 3.

### *Physical and chemical changes in fossil fuels*

Clearly, earth science as a complete subject is beyond the scope of the present paper, so detailed examples of applications are mainly restricted, here to the area associated with hydrocarbon rich fossil fuels. These have, of

GENERAL APPLICATIONS OF TA TO EARTH SCIENCE MATERIALS

THERMAL STABILITY
PHYSICAL CHANGES
DECOMPOSITION
RECOMBINATION
CHARACTERISATION
IDENTIFICATION
EVALUATION
REACTIVITY
CONTENT IN MIXTURES
DETECTION LIMITS
INDUSTRIAL PERFORMANCE
QUALITY CONTROL

Exhibit 3.

DETAILED APPLICATIONS OF T A TO FOSSIL FUELS

ORGANIC CONTENTS
ORGANIC RANK
INORGANIC CONSTITUENTS
CALORIFIC VALUES
COMBUSTION CHARACTERISTICS
PROXIMATE ANALYSIS
SULPHUR CONTENTS
COAL ASH ASSESSMENT
QUALITY CONTROL
ENVIRONMENTAL ASPECTS

Exhibit 4.

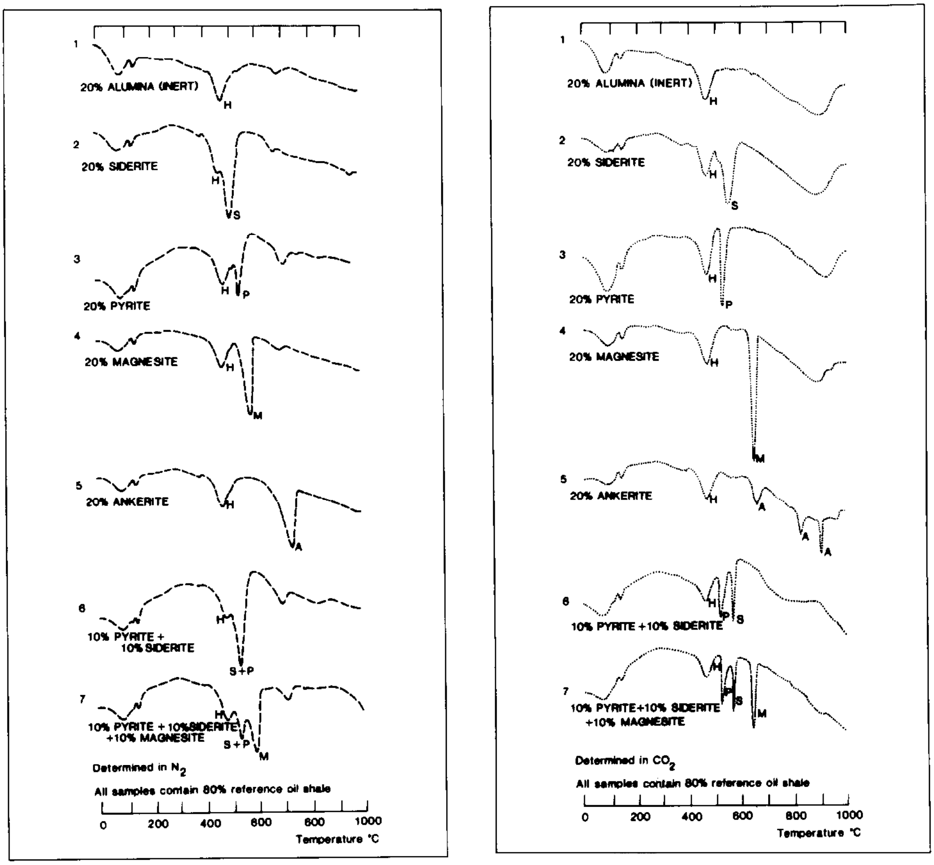

Fig. 2. Two comparative sets of DTA curves determined in furnace atmospheres of $N_2$ and $CO_2$. Duplicate mixtures of oil shale were used with different percentage of minerals or alumina (as labelled). Peaks marked S, P, M, A and H are due to the minerals siderite, pyrite, magnesite, ankerite, and the hydrocarbon yield, respectively. (After Warne and French [32] with permission.)

VARIABLE ATMOSPHERE THERMAL ANALYSIS
OXIDISING CONDITIONS-AIR AND OXYGEN

APPLICATIONS

OXIDATION
COMBUSTION
ORGANIC CONTENTS
MINERAL IDENTIFICATIONS
COAL ASH CONTENT
MAGNETIC COMPONENTS

Exhibit 5.

late, attracted much TA attention and represent well the amount and diversity of research which the earth sciences have attracted (see Exhibit 4).

## *Variable atmosphere thermal analysis*

With the application of this technique individual reactions may be made to: appear earlier or later, be suppressed or enhanced [38], to produce greater sensitivity, give improved detection limits [39], resolution of superimposed peaks [34], mineral identification [34,38,39] (see Fig. 2) organic contents and combustion characteristics [28,40], ash or liquefaction residue analysis or beneficiation determinations [18,35] and pyrite contents [34].

At this point we can consolidate by giving further examples of the types of determination which may be made in the oxidizing conditions of air or $O_2$ (see Exhibit 5) or under inert conditions of $N_2$, $CO_2$ or Ar (see Exhibit 6).

In addition, different purge gas partial pressures, preferentially affect reactions [34] (which may be suppressed or promoted [40]), and promote

VARIABLE ATMOSPHERE THERMAL ANALYSIS
INERT CONDITIONS-PURE $N_2$, Ar AND $CO_2$

APPLICATIONS

PROHIBIT OXIDATION
SUPPRESS REACTIONS
NO OTHER CAS PARTIAL PRESSURES
INCREASED REACTION RESOLUTION
BETTER MINERAL IDENTIFICATION
IMPROVED DETECTION LIMITS
COAL MINERAL CONTENTS
COAL VOLATILE YIELDS
COAL ASH CONSTITUENTS
COAL LIQUIFACTION RESIDUES

Exhibit 6.

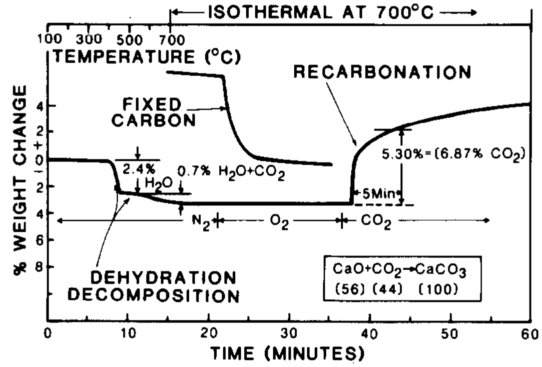

Fig. 3. Multi-gas TG of fluidized bed ash shows two initial weight losses in $N_2$ due to the dehydration of gypsum (2.4%) and the water loss from the hemihydrate + $CO_2$ from calcite (0.75%). Switching to $O_2$ gives a weight loss due to the burning of any fixed carbon present (upper curve), while the final weight gain in $CO_2$ is due to the recarbonation of CaO to form $CaCO_3$. (After Culmo and Fyans, [41] (Figs. 7 and 8) with permission.)

peak identification [23,34], superimposed peak resolution [34] and the identification of any magnetic phases formed [30].

Finally, different sequential gas conditions have been used during individual runs with marked success, e.g. for proximate analysis of coal using $N_2$ followed by $O_2$, i.e. ($N_2$–$O_2$) [40], for preheated coal, bed, fly and fluidized bed ash ($N_2$–$O_2$–$CO_2$) and limestone ($N_2$–$CO_2$) [41] (see Fig. 3), analysis of flue gas scrubber materials after use (flue gas-$N_2$) [42], comparing sulphation, regenerative $SO_2$ and cycle efficiency of sorbents (air–air + $SO_2$–$N_2$–$N_2$ + $H_2$–$N_2$ + air) [43] plus the analysis of solid refuse fuels ($N_2$–$O_2$) [44] and $SO_2$ yield from pyrite contents ($N_2$–$O_2$–$H_2$) [45].

## CONCLUSIONS

It has been clearly demonstrated herein that TA methods and techniques are applicable to a wide range of earth science topics, the scope of which is expanding rapidly and provide data, particularly in circumstances where heating is involved, that is often not readily available from or is complementary to the results from other methods of investigation. In some cases the results are superior to those obtained with other methods, whilst the techniques of simultaneous and variable atmosphere determinations provide considerable additional information which has high potential for materials characterization and industrial process utilization.

## REFERENCES

1 R.C. Mackenzie, A History of Thermal Analysis, Thermochim. Acta, 73 (1984) 251.
2 H. Le Chatelier, C.R. Acad. Sci. Paris, 104 (1887) 1443.
3 H. Le Chatelier, Bull. Soc. Fr. Miner. Crist., 10 (1887) 204.

4 R.C. Mackenzie (Ed.), Differential Thermal Investigation of Clays, Min. Soc. Clay Min. Gp. London, 1957.
5 R.C. Mackenzie, Scifax, Differential Thermal Analysis Data Index, Cleaver-Hume, London, 1962 and Supplement 1964.
6 R.C. Mackenzie, Differential Thermal Analysis, Vol. 1, Fundamental Aspects, Academic Press, New York, 1970; and Vol. 2, Applications, 1972.
7 D. Schultz, Differentialthermoanalyse (Differential Thermal Analysis), VEB Deutscher Verlag der Wissenschaften, Berlin, 1971.
8 W. Smykatz-Kloss, Differential Thermal Analysis—Application and Results in Mineralogy, Springer-Verlag, Berlin, 1974.
9 D.N. Todor, Thermal Analysis of Minerals, Abacus Press, Tunbridge Wells, U.K., 1976.
10 P.D. Garn, Thermoanalytical Methods of Investigation, Academic Press, London, 1965.
11 W.W. Wendlandt, Thermal Analysis, 3rd edn., Wiley, New York, 1985.
12 D. Dollimore (Ed.) Proc. 1st and 2nd ESTA Conferences (Salford, 1976, and Aberdeen, 1981), Heydon and Son, London.
13 D.J. Morgan, J. Therm. Anal., 12 (1977) 245.
14 D.J. Morgan, S.St.J. Warne, S.B. Warrington and P.H.A. Nancarrow, Min. Mag., 50 (1986) 521.
15 D.J. Morgan, S.B. Warrington and S.St.J. Warne, Thermochim. Acta, 135 (1988) 207.
16 K. Rajeshwar, D.B. Jones and J.B. DuBow, Thermochim. Acta, 63 (1983) 97.
17 S.St.J. Warne and P.K. Gallagher, Thermochim. Acta, 110 (1987) 269.
18 C.M. Earnest, Thermal Analysis of Clays, Minerals and Coals, Perkin-Elmer Co., Norwalk, USA, 1984.
19 C.M. Earnest (Ed.), Compositional Analysis by Thermogravimetry, ASTM Special Publication No. 997, Philadelphia, 1988.
20 D.D. Rustschev, Use of Thermal Analysis for Investigating Different Solid Fuels (Invited Review), Therm. Anal. Abs., 18 (1989) 1.
21 K. Heide, Dynamische Thermische Analysenmethoden (Methods of Dynamic Thermal Analysis), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1982.
22 K.H. Wolf, A.J. Easton and S.St.J. Warne, in Carbobate Rocks, Eds. G.V. Chilingar, H.J. Bissell and R.W. Fairbridge, Elsevier, Amsterdam, 1967, pp. 253–341.
23 S.St.J. Warne, in C. Karr, Jr. (Ed.), Analytical Methods for Coal and Coal Products, Academic Press, London, 1979, pp. 447–477.
24 S.St.J. Warne, H.J. Hurst and W.I. Stuart, Therm. Anal. Abs., 17 (1988) 1.
25 S.St.J. Warne and J.V. Dubrawski, J. Therm. Anal., 35 (1989) 219.
26 W.W. Wendlandt, Anal. Chem., 56 (1984) 250R.
27 A.E. Milodowski and D.J. Morgan, in W. Hemminger (Ed.), Proc. 6th ICTA Conf., Bayreuth, Birkhauser Verlag, Stuttgart, 1980, Vol. 2, p. 289.
28 J.W. Cumming and J. McLaughlin, Thermochim. Acta, 57 (1982) 253.
29 J.V. Dubrawski and S.St.J. Warne, Min. Mag., 25 (1988) 627.
30 P.K. Gallagher and S.St.J. Warne, Thermochim. Acta, 43 (1981) 253.
31 M.E. Brown, Introduction to Thermal Analysis—Techniques and Applications, Chapman and Hall, London, 1988.
32 S.St.J. Warne and D.H. French, Thermochim. Acta, 76 (1984) 179.
33 D.J. Morgan, J. Therm. Anal., 12 (1977) 245.
34 S.St.J. Warne and D.H. French, Thermochim. Acta, 79 (1984) 131.
35 C.M. Earnest, Proc. 3rd. Coal Test Conf., Lexington, USA, 1983, p. 66.
36 E. Maxwell, D.R. Kellard, I.S. Jacobs and M.L. Levinson, Fuel, 61 (1982) 369.
37 F. Paulic, J. Paulic and M. Arnold, J. Therm. Anal., 25 (1982) 313.
38 S.St.J. Warne, Thermochim. Acta, 110 (1987) 501.
39 S.St.J. Warne, Nature, 269 (1977) 678.
40 S.St.J. Warne, Thermochim. Acta, 86 (1985) 337.

41 C.F. Culmo and R.L. Fyans, in C.M. Earnest (Ed.), Compositional Analysis by Thermogravimetry, ASTM Special Publication No. 997, Philadelphia, 1988, pp. 245–253.
42 D.L. Dorsey and B.J. Buecker, in C.M. Earnest (Ed.), Compositional Analysis by Thermogravimetry, ASTM Special Publication No. 997, Philadelphia, 1988, pp. 254–258.
43 A.E. Duisterwinkel, E.B. Doesburg, G. Hakvoort, Thermochim. Acta, 141 (1989) 51.
44 R.K. Agrawal, in C.M. Earnest (Ed.), Compositional Analysis by Thermogravimetry, ASTM Special Publication No. 997, Philadelphia, 1988, pp. 259–271.
45 D.M. Aylmer and M.W. Rowe, Thermochim. Acta., 78 (1984) 81.