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Differential Thermal Analysis: The Potential of Controlled Furnace Atmosphere Effects

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Dynamic controlled atmosphere differential thermal analysis (DTA), in which the furnace atmosphere is constantly maintained (by purging gas flows) under preselected conditions, such as oxidising, inert, reducing or of the same composition as the gaseous decomposition or pyrolytic products of the sample under test, provides a valuable technique whereby individual DTA peaks may be suppressed, enhanced, moved up or down the temperature scale or even remain completely unaffected (crystallographic inversions/reversions). Such predictable phenomena can be of considerable value in diagnostic mineralogy, content and composition evaluation of minerals together with increasing the detection limits of species such as carbonates.

Introduction

The rapid expansion of differential thermal analysis (DTA) entered a new phase, one of consolidation, reference data reliability and acceptance, with the publication (1962) of the "SCIFAX, Differential Thermal Analysis Data Index"[1] (subsequently followed by the five volume, Atlas of Thermoanalytical Curves, 1971–76)[2]. Directly relatable to this, a number of investigations have probed the accuracy and reproducibility aspects of DTA. The overall results categorised as the "effects of controllable variables" have been summarised by Bayliss and Warne[3], but surprisingly little has been published concerning their practical and beneficial applications in the field of DTA and particularly with regard to controlled furnace atmospheres of gases other than air.

The following example, the forerunner of other publications, is invoked to highlight the potential practical value and applications of controlled furnace atmosphere DTA.

The detailed paper[4] describes how, complex multi-peaked coal DTA curves previously obtained essentially in atmospheres of their own pyrolytic products[5,6,7] and the large broad exothermic oxidation features produced in static air atmospheres[7] could be reduced to relatively featureless curves by using dynamic nitrogen furnace atmospheres. The mineral siderite, $FeCO_3$, provides another excellent example of the suppression of unwanted peaks when a suitable furnace atmosphere gas is used, Warne[8].

Thus (1) unwanted background or individual interfering peaks produced by single substances, minerals or mixtures may be suppressed or removed by suitable changes in furnace atmosphere conditions.

Individual examples encountered as the investigations have progressed are the coal, above[4], the removal of the exothermic peaks and the endothermic peak of siderite in nitrogen and oxygen atmospheres respectively[8,9] and the almost complete suppression of the interfering oxidation peak of cerussite when determined in argon and carbon dioxide, as compared to air or oxygen (all dynamic), Warne and Bayliss[10].

(2) The decomposition temperature (and related DTA peak) of gas liberating reactions can be raised or lowered by increasing or decreasing the partial pressure of the particular evolving gas in question, in the furnace atmosphere in contact with the decomposing material.

An excellent illustration of this is provided by simple anhydrous carbonate minerals which decompose with a single reaction to liberate all their combined carbon dioxide i.e. $CaCO_3 \rightarrow CaO+CO_2 \uparrow$.

Further DTA work on coal/carbonate mixtures determined in furnace atmospheres of dynamic carbon dioxide gas has resulted in "an improved DTA method for the identification and evaluation of calcite, dolomite and ankerite in coal"; Warne[11], which shows that:-

(a) not only are the "coal" peaks just as well suppressed

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by the "inert" gas, carbon dioxide, as with nitrogen (thus enabling the small mineral content peaks to be resolved and detected),

but

(b) the increased partial pressure of carbon dioxide gas in the latter case also produced reproducible modifications to the peaks caused by the carbonate mineral components of the mixtures.

Thus in carbon dioxide, compared to nitrogen the carbonate decomposition is delayed and occurs with a faster reaction rate and at a higher temperature. As a result the single decomposition peak on the DTA curve moves "up scale" to appear with improved peak definition (due to higher and narrower peaks), and with higher initiation, peak and termination temperatures.

An important exception to point (2) above is exhibited, for example, by the multiple *decomposition* reactions of the carbonate minerals cerussite ($PbCO_3$), Warne and Bayliss[10] and dolomite $CaMg(CO_3)_2$ and ankerite $Ca(Mg,Fe)(CO_3)_2$ Warne[11].

Thus when DTA curves of these minerals, as examples, are determined individually in furnace atmospheres of first nitrogen and then carbon dioxide it is found that:

(3) the various endothermic peaks caused by the different carbon dioxide liberating carbonate decomposition reactions of each mineral exhibit different amounts of peak movement caused by the increased partial pressure of carbon dioxide.

As a result, with the exception of the first and lowest temperature endothermic peak in each case, the remaining peak or peaks moved "up scale" to exhibit the modifications described in (2) above. The initial peak in each case however, became displaced somewhat "*down scale*"[11] or essentially retained its position[10].

The overall effect therefore was a marked drawing apart, or separation, and increased definition of the endothermic peaks.

This particular type of DTA curve modification was a major factor in resolving and detecting the important second or middle endothermic peak:-

(a) of cerussite, which was investigated in detail by Warne and Bayliss[10].

and (b) which is directly relatable to the iron content of the dolomite, ferroan dolomite, ankerite series minerals[8,12].

In the latter case this dynamic carbon dioxide furnace atmosphere technique constitutes a new method for the rapid direct evaluation of the iron content in this isomorphous series[12]. With the exception of chemical analysis this represents an advance on the previous methods which have been summarised by Wolf, Easton and Warne[9]. It also provides a method of distinguishing carbonate iron present in the form of siderite from that present in ankerite/ferroan dolomites, even when in mixtures together[8].

A detailed account of this entitled "Iron Content Evaluation by Differential Thermal Analysis, in the Dolomite, Ferroan dolomite, Ankerite Series", is in preparation for publication elsewhere[12].

Conclusions

This technique as developed and illustrated by the work published[3,4,9,10,11] and to be published[8,12] has special implications in diagnostic, content evaluation and applied/industrial mineralogy because for example the detection limits of the minerals siderite or ankerite and the evaluation of the iron content of members of the dolomite, ferroan dolomite-ankerite series appear to be considerably better than those obtainable by normal laboratory X-ray diffraction determinations.

Attention is therefore drawn to the marked and increased potential of controlled atmosphere DTA in the field of determinative mineralogy.

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