

DESCRIPTIVE OXIDATIVE PROFILES FOR PYRITE
IN THE LOW TEMPERATURE ASH COMPONENT OF COALS
BY DIFFERENTIAL THERMAL ANALYSIS

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INTRODUCTION

There are two forms of FeS_2 which may be present in coals. Pyrite is the cubic modification and marcasite is an orthorhombic form. Marcasite is referred to as the low temperature form. Of the two, pyrite is by far the most abundant in the mineral matter of coals. These sulfur-containing minerals are of special interest from an environmental standpoint since their combustion produces sulfur dioxide gas. The $\text{Fe}_2\text{O}_3(\text{s})$ product of oxidation contributes to the ash material of coals along with combined $\text{SO}_x(\text{g})$ with any existing $\text{CaO}(\text{s})$ in the ash. The amount of iron and its oxidation state influence the ash fusion temperature.

The mechanism of oxidation of pyrite and marcasite in air has been the subject of much study and speculation (1-13). The techniques of differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG) offer direct methods for studying the oxidative behavior of these minerals. Thermal analysis data on the oxidation of sulfides, in general, are somewhat inconsistent. It has already been pointed out by several workers (8,11,13), the factors which seem to be important in such thermal analysis studies are good air circulation in the analyzer, constant experimental conditions, and small sample sizes. Kopp and Kerr (11) have reported that the oxidative peak temperature is lowered with decreasing particle size.

In the course of a detailed thermal analysis study dealing with low temperature ash (LTA) components of several pyrite containing coals from southwestern Illinois and eastern Kentucky, it was observed that the thermal analysis peaks obtained by DTA, TG, and DTG were, in many cases, either altered or shifted when compared to those exhibited by the individual minerals themselves. In the following study, some sample handling techniques, synthetic mineral mixtures, and low temperature ash materials are investigated in an attempt to explain some of these phenomena as observed in dynamic air atmospheres.

EXPERIMENTAL

The pyrite ore used in this study was obtained from Dr. O. Katkins, Department of Geology, University of Pittsburgh at Johnstown (UPJ), Johnstown, PA. A second pyrite specimen was purchased from Wards Natural Science Establishment, Inc. (Rochester, NY). Both the UPJ and Wards specimen were subjected to careful mechanical grinding prior to use. The thermal curve shown for pyrite in Figure 1 of this paper is that of the UPJ specimen.

The high purity marcasite specimen (Iowa, USA) was obtained from F.I. Fiene, Institute for Mining and Mineral Resources (IMMR), University of Kentucky, Lexington, KY. All low temperature ash specimens of this study were also obtained from IMMR. All pyrite estimates given for the LTA specimens were made

using a Phillips Model 3100 X-Ray Diffractometer located at IMMR. The sulfur analysis values for these LTA specimens were obtained using a Perkin-Elmer Model 240C Elemental Analyzer with the Sulfur Analysis Kit. A Perkin-Elmer Model 240DS microcomputer data station was used with the elemental analyzer. These values represent all of the sulfur contained in the LTA specimen except for the small quantity which may be present as calcium sulfate or gypsum.

All DTA thermal curves reported in this work were obtained using a Perkin-Elmer microcomputer-based DTA 1700 High Temperature Differential Thermal Analysis System. Only the DTA mode of operation of this instrument was used in the studies presented here. Ceramic liners (60 mm³) were used in the DTA sample holder cup. However, it was found that platinum liners could also be used with small pyrite samples and with all LTA specimens of this study in dynamic air purge. In these cases, the pyrite oxidation is complete prior to the decomposition temperature for pyrite.

RESULTS AND DISCUSSION

Pyrite and Marcasite Specimens

In this study, both pyrite and marcasite specimens exhibited broad multi-step DTA oxidative profiles when DTA samples of approximately 21 milligrams were studied in an undiluted fashion. The temperature of initiation of the exothermic activity was ca. 360°C when the specimens were heated at 10°C per minute. The temperature range of the exothermic oxidative profile was found to be highly dependent upon sample size and heating rate. Smaller sample sizes and slower heating rates gave oxidative profiles which were more singular in nature for these undiluted samples.

Dilution of the pyrite or marcasite with alumina or inert material allows a better oxidant availability to the sample material and more closely simulates the distribution of pyrite in natural specimens such as the LTA component of coals. Figures 1 and 2 give the DTA oxidative thermal curves for diluted samples of pyrite and marcasite, respectively. As one can see, very similar oxidative profiles are obtained for these diluted specimens. The major difference which was observed in these studies is that the sharp exothermic peak maximum for the FeS₂/Al₂O₃ mixture was, on the average, 25°C lower in temperature for the marcasite specimens than the pyrite specimens of this study. No such difference was observed for the broad exothermic profiles associated with the larger undiluted samples.

Herrin 6 LTA Specimen

The oxidative profiles for the pyrite component of low temperature ash materials from coals are somewhat different from those given for pyrite and marcasite in Figures 1 and 2. The DTA thermal curve, shown in Figure 3, is that which was obtained for a LTA specimen of the Herrin 6 seam (southwestern Illinois). As one can see, a multi-step exothermic oxidative region with peak maxima at 407°C, 464°C, and 508°C is obtained. This LTA specimen was analyzed to contain 9.9% sulfur and the pyrite and marcasite content was estimated by XRD to be 19% and 2%, respectively. Since this coal was subjected to low temperature ashing in an oxygen plasma where temperatures near 100°C are reached, the presence of considerable iron sulfates is likely. This turns out to be the case as is described in a paper (17) which follows this writing. Rao and Gluskoter (14) found the iron sulfates content in 44 specimens of the Herrin 6 seam to vary from 0 to 32 percent. In general, however, the iron sulfate minerals rarely comprised more than 7 percent of the LTA matter for the Herrin 6 seam.

Pyrite/Iron Sulfate/Al₂O₃ Synthetic Mixture

Since ferrous sulfate is known to be the intermediate step in the total oxidation of pyrite (4), a study was performed to determine the effect of the presence of iron (II) sulfates on the oxidative profile of pyrite. Figure 4 shows the resulting DTA, TG, and DTG oxidative thermal curves obtained from a synthetic mixture containing 23.1% pyrite, 13.76% FeSO₄·H₂O, and 63.1% Al₂O₃ diluent were heated at 10°C per minute in dynamic air atmosphere. Although not labeled in the DTA thermal curve, the exothermic region gives peak maxima at 465°C and 520°C with a relative minimum separating these at 478°C. The endothermic event beginning near 600°C is the normal ferrous sulfate decomposition as observed in dynamic air atmosphere (16). When this DTA pattern is compared with that observed in Figure 1 for the pyrite/Al₂O₃ mixture, one will note that the presence of iron sulfates lowers the temperature of the major peak maximum by 27°C and also converts the oxidative profile to a clearly defined two stage event. One will note that the peak maximum at 465°C is in common with that in the LTA material for the Herrin 6 seam which gives a maximum at 464°C. The TG and DTG thermal curves in Figure 4 show that the exothermic peak at 465°C is associated with a weight gain and the one at 520°C is associated with a weight loss event. It should be pointed out that the pyrite/iron sulfate synthetic mixture exhibits an iron sulfate decomposition above 600°C while the thermal curves for pyrite/Al₂O₃ mixture did not.

Variation of the Pyrite Exothermic Response with Pyrite Level in LTA Specimens

A study was performed to see how the oxidative profile varied with the pyrite level in a series of LTA ash specimens. For this study, LTA specimens from the Herrin 6 seam (southwestern Illinois), Hazard 8 seam (eastern Kentucky), and two specimens of the Hazard seam from two different locations in eastern Kentucky. Table I gives the estimated pyrite levels for three of the four LTA specimens as obtained by XRD techniques. The total sulfur, as assigned by the Perkin-Elmer 240C Elemental Analyzer, is also given for the LTA specimens. As one can see, the pyrite level varies from as high as 19% in the Herrin 6 specimen to a low of 2% in the Hazard 7 LTA specimen.

Figure 5 shows the DTA oxidative thermal curves obtained for these LTA specimens in a dynamic air purge of 50 cc/min. The sample weights used were 23.1 mg for the Herrin 6, 35.0 mg in the Hazard 8, 29.5 mg in the Hazard 7, and 28.7 mg of the Hazard 7A LTA specimen. One will immediately note that the middle exothermic event (T_{max} = 464°C) in the Herrin 6 specimen is in common with the other 3 specimens. This event is observed at 464°C in the Hazard 8 LTA specimen and at 459°C in the Hazard 7A specimen. One will recall that this peak was also observed at 465°C in the synthetic pyrite/FeSO₄ mixture. The temperature of this peak maxima decreases as the amount of pyrite decreases and thus occurs at 438°C for the Hazard 7 specimen which was estimated to contain only 2% pyrite.

From these thermal curves one might predict that the exothermic oxidative profiles become multi-peaked and show activity at higher temperatures as the pyrite level increases. This is in agreement with our previous experiments given earlier in this work. The temperature of onset of oxidation is very similar in all four of the LTA specimens even though the mineral content of the Illinois coal is quite different from the three Kentucky coal LTA specimens. All four LTA specimens contained significant iron sulfate component. This iron sulfate level being less as the pyrite level decreases. This may be seen by the

decrease in magnitude and temperature of the decomposition peak observed at 667°C in the Herrin 6, 662°C in the Hazard 8, etc. This endothermic peak, in some cases, overlaps and predominates over less intense illite-smectite or smectite clay mineral dehydroxylation in these low temperature ash specimens.

The clay mineralogy was noticeably different in the four LTA specimens. For example, all three of the Kentucky coals contained detectable levels of kaolinite, as is evidenced by the exothermic ordering peak (spinel formation) at 968°C, 976°C, and 984°C in the Hazard 8, Hazard 7, and Hazard 7A, respectively. The Herrin 6 seam showed no evidence of kaolinite at the level of detectability of DTA. The double endothermic peak at 108°C and 150°C in the Herrin 6 specimen is due to the loss of interlayer water from both illite and illite-smectite mixed layer clay minerals. The lower temperature event (108°C) may also be due, in part, to the dehydration of iron sulfate species such as the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite), $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite), and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (coquimbite). Likewise, the endothermic peaks in the Hazard 8 (113°C), Hazard 7 (111°C) and Hazard 7A (113°C) specimens are due to the same water loss phenomena. Because of the fact that the Hazard 7 specimen contains very little iron sulfate component, the thermal curves for the three Kentucky specimens indicate that these endothermic events are mostly due to the presence of illite and mixed layer clays containing illite clay mineral.

The Herrin 6 contained a measurable calcite component while the three Kentucky specimens did not. The endothermic peak at 890°C in the DTA thermal curve for the Herrin 6 seam is associated with the decomposition of calcite although it is sharpened by its association with the oxidation products of the pyrite. This will be discussed in detail in a paper which follows (17). One will also note that the clay mineral dehydroxylation endotherm (ca. 540°C) which is observed immediately after the pyrite oxidation is more distinguishable in the Hazard 7 and 7A specimens than in the Hazard 8 specimen. This is primarily due to the lower kaolinite and higher pyrite level in this specimen than is present in the two Hazard 7 specimens.

CONCLUSION

The temperature range as well as the nature of the exothermic oxidative profile for pyrite was found to be highly dependent upon sample size and heating rate. Smaller sample sizes and slower heating rates favor a more singular oxidative profile. Dilution of the pyrite or marcasite specimen with alumina or inert material allows a better oxidant availability to the sample material and more closely simulates the distribution of pyrite in natural specimens such as LTA specimens from coals.

The presence of iron sulfates lowers the peak temperature and converts the oxidative profile for pyrite specimens to a two stage event. Furthermore, pyrite specimens, as well as LTA specimens from coals, containing significant levels of iron sulfates were observed to exhibit a DTA endothermic event between 630°C and 670°C which is characteristic for the decomposition/oxidation of the iron sulfates component. This thermal event was absent from the DTA oxidative thermal curves for pyrite samples which initially contained no iron sulfates.

The DTA oxidative profiles for LTA specimens containing varying amounts of pyrite and iron sulfates showed that the exothermic oxidation of the pyrite component becomes more multistep in nature as the pyrite level increases. The iron sulfate content of the LTA material was observed to increase with the pyrite in the same specimen. This was reflected in the DTA thermal curves by the magnitude of the endothermic thermal event near 660°C. In the LTA specimens of this study, this iron sulfate decomposition/oxidation endotherm near 660°C in the DTA thermal

curve was observed to overlap and, in some cases, mask the less intense endothermic dehydroxylation peak of mixed layer clays which contain smectite clay mineral components.

ACKNOWLEDGMENTS

The author would like to express his sincere appreciation to F.I. Fiene for both the low temperature ash specimens and supporting XRD results. He would also like to thank R.F. Culmo and Kathy Weisgale for performing the sulfur analyses which were presented in this work.

REFERENCES

1. R.C. MacKenzie, "The Differential Thermal Investigation of Clays", Mineralogical Society, London, 1957, p. 366.
2. J.R. Blachere, J. Am. Ceram. Soc., 49 (1966) 590-593.
3. L.G. Berg and E.N. Shlyapkina, J. Thermal Anal., 8 (1975) 329-337.
4. A.C. Banerjee, in Thermal Analysis ICTA 80 Vol. 2 (W. Hemminger, Editor), Birkhaeuser Verlag, Basel, 1980, pp. 241-246.
5. Nandita Chakrabarti, D.R. Glasson, and S.A.A. Jayaweera, Thermochim. Acta, 51 (1981) 77-84.
6. R. Dimitrov and B. Boyanov, Thermochim. Acta, 64 (1983) 27-37.
7. D.N. Todor, Thermal Analysis of Minerals, Abacus Press, Kent, 1976, 116-117.
8. E.M. Bollin, in Differential Thermal Analysis, Vol 1 (R.C. MacKenzie, Editor), Academic Press, London, 1970, p. 193.
9. Haw-Jye Shyu, P.O. Vaishnava, and P.A. Montano, Fuel, 60 (1981) 1022-1026.
10. G.M. Schwab and J. Philinis, J. Am. Chem. Soc., 769 (1947) 2588.
11. O.C. Kopp and P.F. Kerr, Am. Miner., 43 (1958) 1079.
12. R.A. Schloenlaub, J. Am. Cer. Soc., 52 (1969) 40.
13. T. Kennedy and B.T. Sturman, J. Thermal. Anal., 8 (1975) 329-337.
14. C.P. Rao and H.J. Gluskoter, "Occurrence and Distribution of Minerals in Illinois Coals", Illinois Geological Survey Circular 476, Urbana, Illinois, 1973.
15. F.W. Frazier and C.B. Belcher, Fuel, 52 (1973) 41.
16. P.K. Gallagher, D.W. Johnson, and F. Schrey, J. Amer. Ceram. Soc., 53 (1970) 666.
17. C.M. Earnest, in preparation.

Table I

Pyrite and Total Sulfur Content
For The
Four LTA Specimens Of This Study

<u>LTA Specimen</u>	<u>Pyrite (XRD Estimate)</u>	<u>% Total Sulfur</u>
Herrin 6	19%	9.9
Hazard 7	2%	1.7
Hazard 7A	5%	3.8
Hazard 8	NA	6.5

NA = Not Analyzed

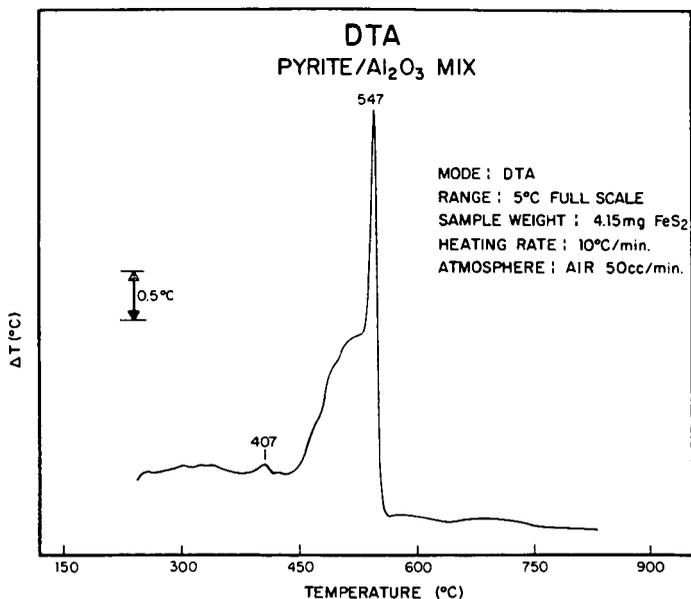


Figure 1. DTA Oxidative Thermal Curve for Pyrite/Al₂O₃ Mixture
Containing 4.15 mg of Pyrite

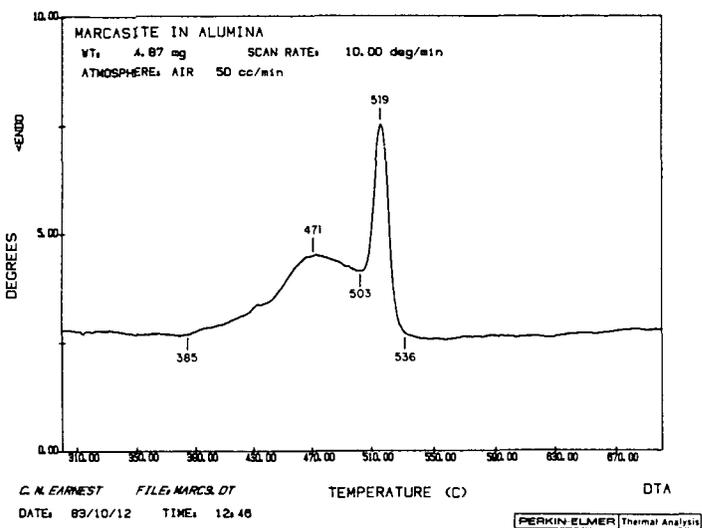


Figure 2. DTA Oxidative Thermal Curve for a Marcasite/ Al_2O_3 Mixture Containing 4.87 mg of Marcasite

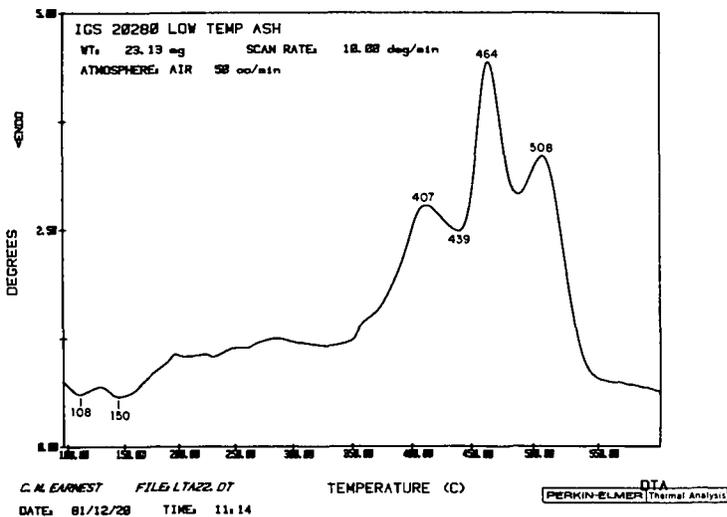


Figure 3. DTA Thermal Curve for Low Temperature Ash Component of the Herrin 6 Seam in Dynamic Air Atmosphere

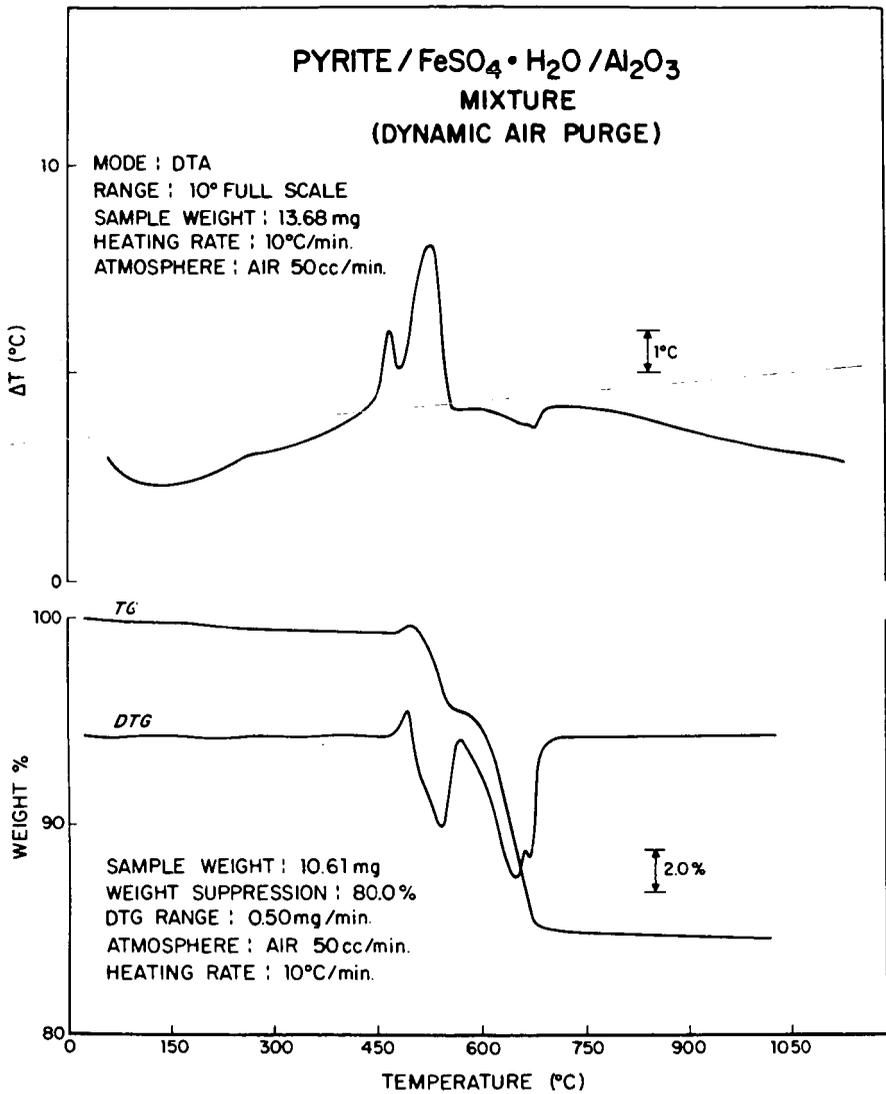


Figure 4. DTA, TG, and DTG Thermal Curves for Pyrite/
 $\text{FeSO}_4 \cdot \text{H}_2\text{O} / \text{Al}_2\text{O}_3$ Synthetic Mixture

DTA-1700
LOW TEMPERATURE ASH
(DYNAMIC AIR ATMOSPHERE)

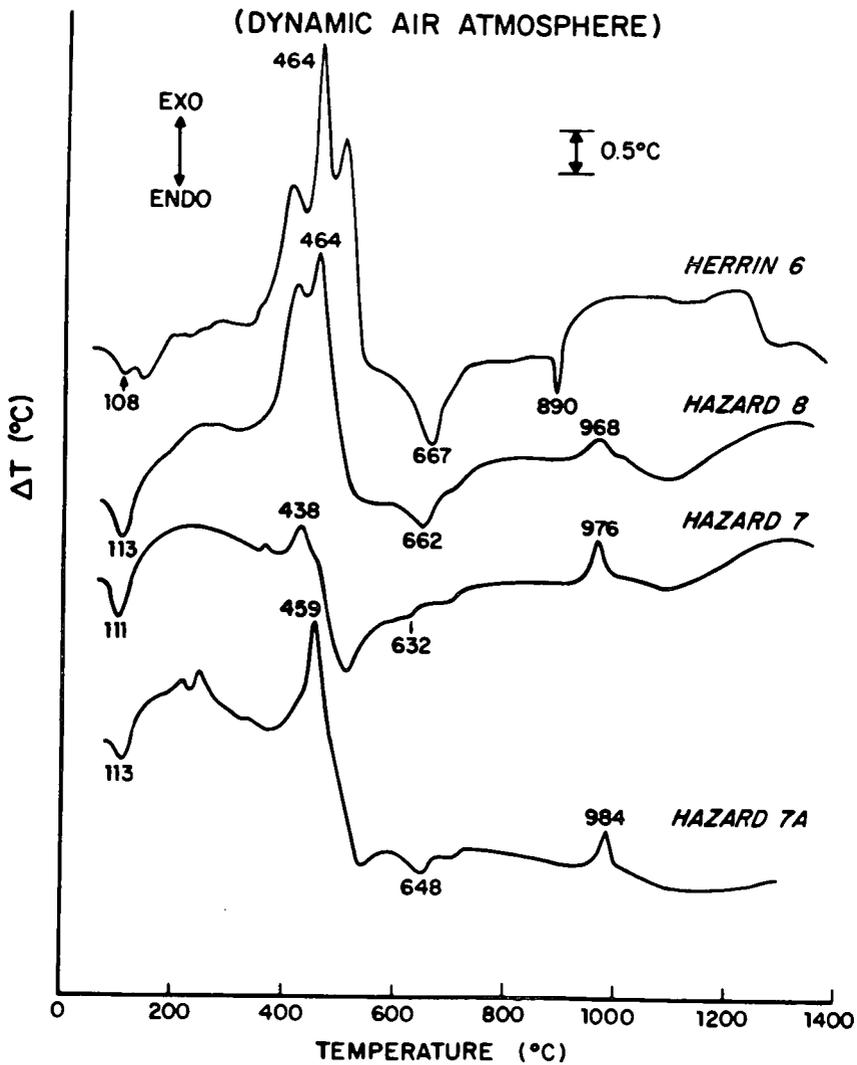


Figure 5