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DIFFERENTIAL THERMAL ANALYSIS OF SULFIDES AND ARSENIDES

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ABSTRACT

Minerals containing corrosive elements such as sulfur and arsenic present unusual difficulties when subjected to differential thermal analysis. The reaction products often attack and destroy thermocouples, and the sample block is frequently corroded. A method has been developed by this laboratory to overcome this difficulty which consists primarily of protecting the metal differential thermal head and thermocouples with thin-walled alundum cylinders. Also, a slight modification of the furnace prevents the gaseous products from coming into contact with the heating coils.

The equipment appears to be sensitive to both exothermic and endothermic reactions. The reactions are generally of large magnitude so a sample to inert filler ratio of about 1:15 gives good results in most cases.

The method may be applied to several mineral groups which have been generally omitted from differential thermal studies. Its primary value may lie in the rapid identification of small quantities of ore minerals. Further investigation may show that quantitative as well as qualitative data may be obtained and combined with x -ray study, crystal structures and the effects of substitution may be better understood. Several illustrative differential thermal curves of minerals containing sulfur and arsenic are shown, including pyrite, chalcopyrite, arsenopyrite, sulfur and arsenic.

INTRODUCTION

Differential thermal analysis is essentially a non-equilibrium study of the endothermic and exothermic reactions a material undergoes when heated over a particular temperature range. The conception of the method is attributed to Le Chatelier (1887). Apparently little application was made until the 1930's when workers such as Orcel and Caillère (1933), Insley and Ewell (1935) and Norton (1939) showed the value of the technique. Most of this early work was done on clay minerals which give good reactions for water loss and the formation of gamma Al_2O_3 . Other minerals which have received the attention of several investigators are the carbonates. Cuthbert and Rowland (1947), Kerr and Kulp (1948), Beck (1950) and others have successfully applied differential thermal

analysis to the carbonate minerals. Hydrous minerals, oxides, metamict minerals, micaceous minerals and even coals have been subjected to differential thermal analysis. In general, however, there has been a tendency to avoid the mineral groups containing corrosive elements such as sulfur and arsenic. The authors know of only one published work dealing specifically with thermal analysis of sulfides (Hiller and Probsthain, 1955).

Hiller and Probsthain (1955) have shown that it is possible to apply differential thermal analysis to the sulfides. They used a ceramic head and made the analyses in an inert atmosphere. The authors state that a disadvantage of the method is the lack of response of the apparatus to exothermic reactions.

The method developed by this laboratory permits the samples to be heated in air, taking advantage of the possible oxidation reactions which are generally large. The apparatus which is described below appears to be sensitive to both endothermic and exothermic reactions. The program controlling device and recorder have been described by Kerr and Kulp (1948, 1949). The thermal head has been redesigned to permit the use of thin-walled alundum cylinders which protect the metal head and thermocouples from corrosion. The furnace has been altered slightly to allow the gaseous reaction products to escape without coming into direct contact with the heating coils.

DESCRIPTION OF THE APPARATUS

The differential thermal head is illustrated in Fig. 1. It is made of 18-8 chrome nickel steel and finished to the dimensions shown. Four equally spaced wells are provided. At present only one of these is used as a reference well, and the others are used one at a time as sample wells. It is also possible to run two samples simultaneously. The alundum cylinders used to protect the head and thermocouples are commercially available and come in a number of sizes. The sizes used are: $\frac{1}{2}$ " O.D. \times $7/16$ " I.D. \times $\frac{1}{2}$ " long for the outer protective cylinder, and $\frac{1}{4}$ " O.D. \times $3/16$ " I.D. \times 1" long for the inner protective cylinder. The outer cylinder protects the metal head while the inner one protects the thermocouple of each well. In order to better accomplish this, the inner cylinder is fitted into a recess extending $\frac{1}{4}$ " below the level of the well bottom. The alundum cylinders may be easily replaced if contaminated or broken.

Two other modifications simplify the repair of thermocouples when necessary. First, the thermocouples are not cemented in place but held by asbestos which is forced into the space between the alundum tubing used in the construction of the thermocouples and the metal head. It has been found that this tends to eliminate breakage of the alundum tubes at the contact. Second, the method of preparation of thermocouples has been

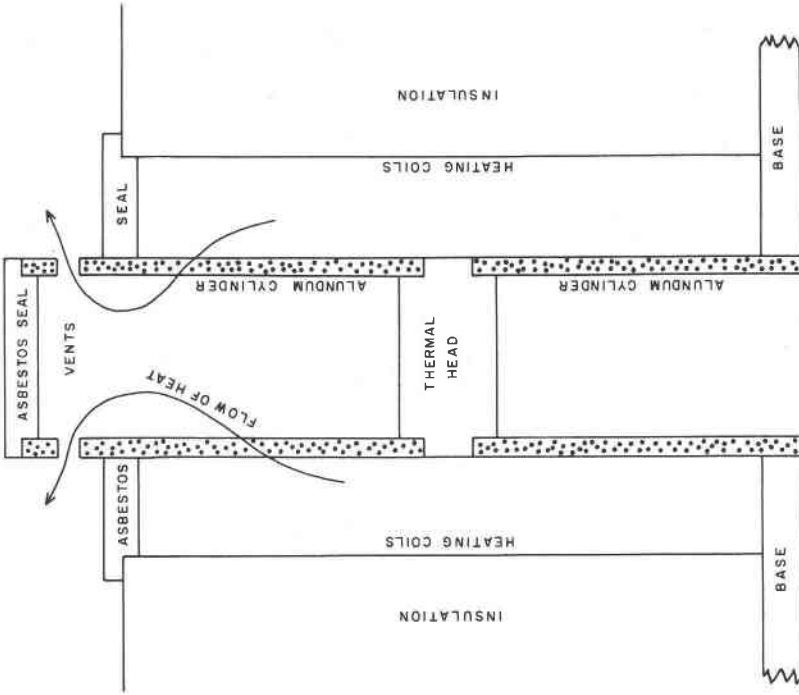


Fig. 2. Diagrammatic sketch of thermal head mount.

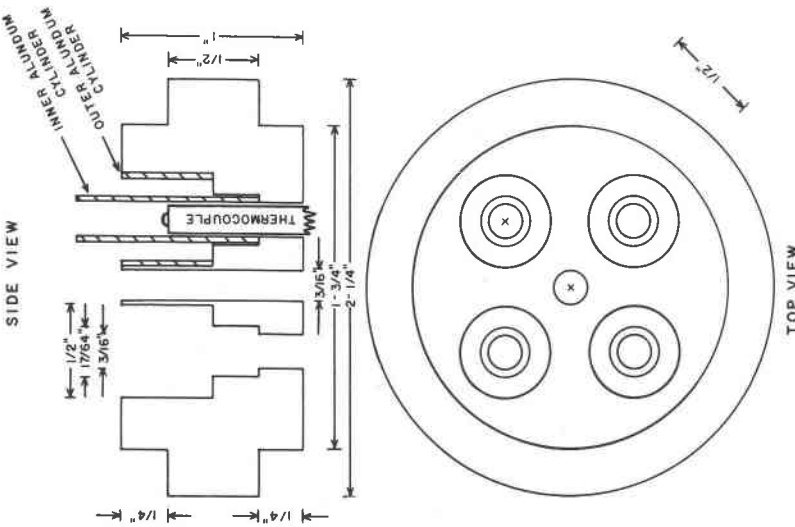


Fig. 1. Thermal head.

improved. Formerly the common (alumel) wire of a thermocouple pair consisted of one piece of wire joining the thermocouples. Individual thermocouples of chromel and alumel are now made, the alumel leads being connected in a mercury junction.

Figure 2 illustrates the position of the thermal head within the furnace and the method employed to prevent the gaseous reaction products from coming into direct contact with the heating coils. The permeable alundum cylinders which support the head and also provide a flue for corrosive gases have the following dimensions: $2\frac{1}{4}$ " O.D. \times $1\frac{3}{4}$ " I.D. The lower supporting cylinder is of sufficient length to center the head within the furnace, and the upper vented cylinder to extend approximately 3" above the furnace top. Since the rate of heat flow is somewhat inhibited at the start of a run, automatic program controlling must be deferred until the rate of temperature increase reaches about 12.5° C./minute.

PROCEDURE

The inner alundum cylinders of both sample and standard wells are filled with 120 mesh alumina. The space between inner and outer alundum cylinders is completely filled with 60 mesh alumina in the standard well, but to only one-fifth the height of the sample well. The remaining volume is loaded with an intimate mixture of sample and 60 mesh alumina. The optimum sample grain size has not yet been determined. However, in the present work the powders have been finer than 100 mesh. Several sample:alumina ratios have been used from 1:3 to 1:20 by volume. One part of sample in fifteen parts of inert filler (alumina) appears to yield good results for most of the sulfides and arsenides tested. Subsequent detailed study should reveal the grain size and ratio which yield the best results. The sample:alumina ratio may be found to be expressed more accurately in terms of weight than volume. It is believed that the ratio range expressed above indicates the approximate limits of the sample-inert filler mixture. If the ratio is greater than 1:3 it is often difficult to remove the reaction products from the sample well, and the reactions may be too large to record accurately. If the ratio is less than 1:20 it may be necessary to amplify the record excessively to distinguish weak reactions.

The reactions of samples are compared to standard alumina following the procedure for normal non-corrosive materials. This comparison is made from room temperature to 1000° C., the rate of temperature increase being standardized at 12.5° C./minute. Automatic temperature control is possible once this heating rate is attained.

DIFFERENTIAL THERMAL CURVES OF ILLUSTRATIVE MATERIALS

Thermal curves (Figs. 3, 4) obtained utilizing this equipment are shown for quartz, kaolinite, and several minerals containing sulfur and arsenic. Consistent curves are obtained from repeated trials using the same specimen under uniform test conditions. During an earlier stage in the development of the equipment, the thermocouples required replacement twice because of contamination. At that time the recess into which the inner alundum cylinder extends was added, and no corrosion has been observed subsequently. A list of the significant exothermic and endothermic peaks is shown in Tables 1 and 2.

Quartz

Crushed beach sand was used for this analysis. While minor amounts of heavy minerals may be present, sulfides, arsenides and clay minerals are apparently absent. Only one peak at 580° C. (endothermic) was recorded with a peak height of about one-half inch. The inversion temperature recorded by standard differential thermal equipment is also about 580° C. The equilibrium temperature for the alpha-beta inversion is approximately 573° C. (Keith and Tuttle, 1952).

Kaolinite

Kaolinite from Murfreesboro, Arkansas, yields an endothermic reaction at 610° C. and an exothermic reaction at 990° C. Material from the same locality analyzed by the standard method has corresponding peak temperatures of 605° C. and 995° C. The peak heights recorded by the equipment described compared with the peak heights observed on standard equipment appear to indicate that the new apparatus is somewhat more sensitive to exothermic reactions.

Arsenic

Three exothermic peaks are observed for arsenic from Andreasberg, Harz, at 265° C., 480° C. and 580° C. A study of the material from Andreasberg must necessarily precede any interpretation of the thermal curve obtained since the possibility of contamination with other arsenides and sulfides exists. At least two oxidation reactions of native arsenic are possible: that yielding the tri-oxide and that producing the penta-oxide. It would appear that both reactions would be exothermic. No large endothermic peak resulting from the sublimation of arsenic oxide is observed. This reaction may be of small magnitude or may be concealed by other reactions.

Arsenopyrite

One exothermic reaction at 530° C. is noted for arsenopyrite from Del Oro, Canada. Both sulfur and arsenic are essential constituents of arsenopyrite; hence, it might appear that two or more peaks should be observed. Possibly more data would be obtained with a larger sample: alumina ratio. The curve illustrates a ratio of 1:15. Another possibility is that the reactions occur within the same temperature range, and therefore only a single peak appears.

Chalcopyrite

One exothermic peak at 450° C. and two endothermic peaks at 750° C. and 790° C. are noted for chalcopyrite from Sudbury. The peak at 450° C. represents part of a broad exothermic reaction starting at about 380° C. and gradually diminishing in intensity until it merges with the first endothermic reaction at 750° C. There is a similarity of this broad reaction to the first pyrite reaction (illustrated in Fig. 4). Detailed analysis of the original material and subsequent reaction products should aid the explanation of these observed peaks.

Sulfur

Sulfur from Sicily yields two thermal reactions. The first occurs at 130° C. (endothermic) and represents the melting of the sulfur. A second peak takes place at 380° C. (exothermic) and results from the oxidation of sulfur to sulfur dioxide. The rapid return of the curve to the baseline upon completion of oxidation is probably due to the complete removal of the reaction products as gases.

The initial endothermic peak representing the melting point is of particular interest. The reader may consider some of the peaks illustrated for other materials as relatively broad. Under non-equilibrium conditions sulfur should melt within a short temperature range. The interval recorded is about fifteen degrees, and the peak is quite sharp. It is concluded that the apparatus is capable of recording reactions which occur rapidly, and hence where broad peaks are observed they are due to the nature of the reactions rather than physical effects of the apparatus.

Sphalerite

A single peak at 690° C. (exothermic) occurs for sphalerite from Ellen-ville, New York. This peak represents the combined reactions of the dissociation of the sulfur, its oxidation and the oxidation of the zinc and any iron present. Apparently the latter reactions cannot occur until the dissociation begins. The effect upon peak temperature of the iron content appears to deserve further consideration.

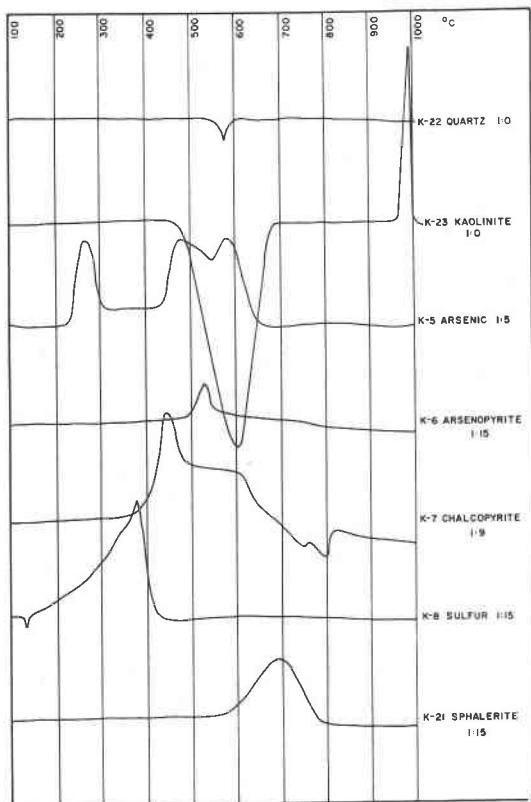


FIG. 3. Thermal curves for quartz, kaolinite and several minerals containing sulfur and arsenic. Sample data are listed in Table 1. (10 \times amplification)

Pyrite

Thermal curves of pyrite from six localities are illustrated in Fig. 4 to show the effect of sample:alumina ratio upon the record and also to indicate the similarities and variations for different specimens of the same species.

The first three curves illustrate the effect of sample dilution. Pyrite from Bingham, Utah (sample K-1) was mixed in the proportions 1:4, 1:8 and 1:15. With decreasing amounts of sample the following is observed:

- The endothermic reactions shown by all samples at approximately 580°C. and 680°C. for a 1:4 ratio do not appear when the sample:alumina ratio is decreased to 1:8 or 1:15.
- The temperature range of the broad exothermic reaction decreases.
- The peaks shift to lower temperatures.

It is possible that the thermal curves produced by a 1:4 mixture of sample and alumina consist essentially of two exothermic peaks. The

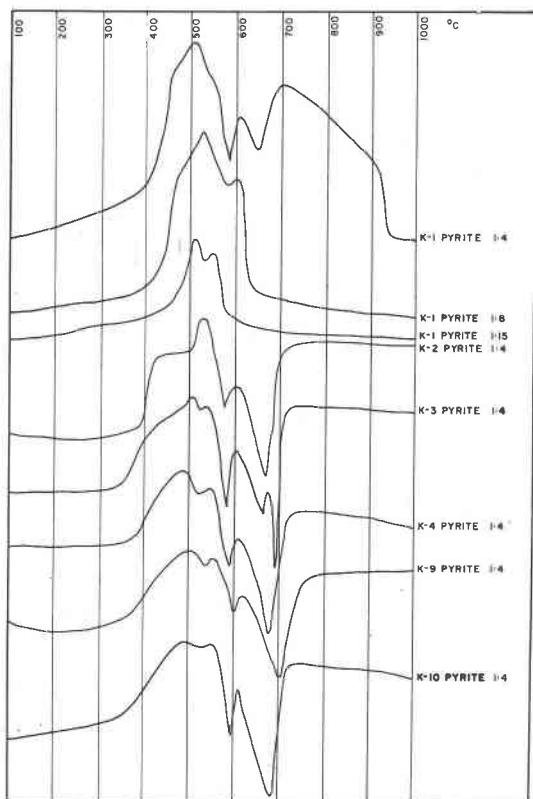


FIG. 4. Thermal curves for pyrite from several localities. Sample data are listed in Table 2. (10X amplification)

first would extend from about 400° C.-580° C. (broad) and the second would be relatively sharp at approximately 610° C. The peak shift would be as follows:

<i>Sample:alumina ratio</i>	<i>First Peak</i>	<i>Second Peak</i>
1:4	400-580° C. (Broad)	610° C.
1:8	440-575° C. (Broad)	600° C.
1:15	460-525° C. (Broad)	550° C.

Another possibility is concerned with the amount of sample present. When the sample:alumina ratio is high, i.e. 1:4, it follows that large amounts of reaction products will form. Perhaps these reaction products will alter the reaction rate and peak temperatures, and may even introduce secondary reactions by surrounding the material with an atmosphere other than air.

The authors intend to investigate pyrite more thoroughly to determine whether one of the above produces the observed phenomena or whether an alternate explanation exists.

TABLE 1. DATA FOR FIGURE 3

Sample Number	Mineral	Locality	Sample:Alumina Ratio	Peak Temperatures (° C.) Reaction Type
K-22	Quartz	Beach Sand	1:0	580 ↓
K-23	Kaolinite	Murfreesboro, Ark.	1:0	610 ↓ ; 990 ↑
K-5	Arsenic	Andreasberg, Harz	1:5	265 ↑ ; 480 ↑ ; 580 ↑
K-6	Arsenopyrite	Del Oro, Canada	1:15	530 ↑
K-7	Chalcopyrite	Creighton Mine, Sudbury	1:9	(380-620) ↑ ; 450 ↑ ; 750 ↓ ; 790 ↓
K-8	Sulfur	Girgenti, Sicily	1:15	130 ↓ ; 380 ↑
K-21	Sphalerite	Ellenville, New York	1:15	690 ↑

TABLE 2. DATA FOR FIGURE 4

Sample Number	Mineral	Locality	Sample:Alumina Ratio	Peak Temperatures (° C.) Reaction Type
K-1	Pyrite	Bingham, Utah	1:4	(400-550) ↑ ; 510 ↑ ; — ; 580? ↓ ; 610 ↑ ; — ; 650 ↓
			1:8	(440-550) ↑ ; 530 ↑ ; — ; 575? ↓ ; 600 ↑ ; — ; — ; —
			1:15	(460-525) ↑ ; — ; 535? ↓ ; 550 ↑ ; — ; — ; — ; —
K-2	Pyrite	Leadville, Colo.	1:4	(390-550) ↑ ; 530 ↑ ; — ; 580? ↓ ; 605 ↑ ; — ; 670 ↓
			1:4	(350-550) ↑ ; 510 ↑ ; 540 ↑ ; 585? ↓ ; 610 ↑ ; 670? ↓ ; 680 ↑ ; 690 ↓
K-3	Pyrite	Isle of Elba	1:4	(380-560) ↑ ; 490 ↑ ; 550 ↑ ; 590? ↓ ; 610 ↑ ; — ; — ; 685 ↓
K-4	Pyrite	Brazil	1:4	(380-585) ↑ ; 500 ↑ ; 550 ↑ ; 600? ↓ ; 620 ↑ ; — ; — ; 700 ↓
K-9	Pyrite	Chile	1:4	(360-570) ↑ ; 480 ↑ ; 550 ↑ ; 590? ↓ ; 610 ↑ ; — ; — ; 680 ↓
K-10	Pyrite	Central City, Colo.	1:4	(360-570) ↑ ; 480 ↑ ; 550 ↑ ; 590? ↓ ; 610 ↑ ; — ; — ; 680 ↓

↑—Peak direction exothermic; ↓—Peak direction endothermic; (380-560)—Broad reaction; ?—Peak may result from overlap of two consecutive peaks in same direction, rather than represent true reaction.

In general, the six samples illustrated in Fig. 4 show similar curves with minor variations. The initial peak is rather broad, extending from about 400° C.–560° C. followed by several endothermic and exothermic peaks listed in Table 2. The variations may provide information concerning the effects of substitution, crystallite size and other crystal data. In such a study precise control of grain size, sample:alumina ratio and sample purity are important. Of the samples illustrated, K-3 from Elba appears to deviate the most from the other curves.

CONCLUSION

The purpose of this paper has been to describe improved equipment for the investigation of minerals containing corrosive elements such as sulfur and arsenic. Differential thermal analysis, while widely used for the examination of materials containing non-corrosive constituents, has been generally avoided where corrosive elements are present. The equipment described appears to overcome this difficulty. Curves have been obtained from as little as 0.15 gm. of pyrite and 0.08 gm. of sulfur. The thermocouples appear to stand up well under repeated use.

The possible application in quantitative determination is suggested by progressively decreasing peaks related to decreasing sample:alumina ratio noted in the case of pyrite from Bingham, Utah. Variations in peak temperatures for corresponding reactions of several specimens of the same mineral, as illustrated by thermal curves for pyrite from six localities, may result from contamination, ionic substitution or mixed crystals.

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