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# THERMOANALYTICAL EXAMINATION OF SAMPLES FROM WABUSH IRON ORE ON BEHALF OF DR. S. R. RAO, POSTDOCTORATE FELLOW

by

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SUMMARY OF RESULTS

Six Wabush Iron Ore samples that were the products of various separation techniques were received from the Mineral Processing Division in early March, 1972, for thermal analysis. The main constituents of the samples were identified as quartz, limonite, hematite, and magnetite; an estimate was made of their relative abundances in the various samples.

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CONTENTS

	<u>Page</u>
Summary of Results .....	i
Introduction .....	1
Experimental Techniques .....	2
(A) Differential Thermal Analysis .....	2
(B) Thermogravimetric Analysis .....	2
Experimental Results and Discussion .....	3
References .....	8
Figures 1 to 4 .....	9 to 12

## INTRODUCTION

In early March, 1972, a request was received from Mr. L. L. Sirois, Head, Metallic Mineral Research Laboratory, Mineral Processing Division, to have thermoanalytical work done on six Wabush Iron Ore samples on behalf of Dr. S. R. Rao, Postdoctorate Fellow. The samples, products of separation processes, were subjected to Differential Thermal Analysis (DTA) and to Thermogravimetric Analysis (TGA) in the Physical Chemistry Group, Mineral Sciences Division.

This report deals with the work done on these samples and outlines the results obtained and the conclusions drawn therefrom.

Table 1 lists the samples and the description supplied with them.

TABLE 1

Wabush Iron Ore Samples

Sample	Description Provided
1	+500-mesh head sample
2	-400-mesh head sample from spiral tails
3	-400-mesh iron ore table tailings
4	-400-mesh iron ore table concentrate I
5	-400+500-mesh iron ore table concentrate II
6	-400+500-mesh iron ore table tailings

NOTE: The samples, as received, all appeared to have aggregated to a greater or lesser degree so that the mesh sizes quoted above were not very meaningful at the time of examination.

Attention is drawn to Mineral Sciences Division Internal Report MS 72-3 by R. G. Pinard<sup>(1)</sup> in which a mineralogical examination was made of a related sample of this ore that appears to be the same as Sample #3 in Table 1 of this report. The work detailed in that report covered the mineralogical examination of various specific-gravity fractions obtained from this sample. There is some measure of disagreement between the findings in that report and those given herein.

## EXPERIMENTAL TECHNIQUES

### (A) Differential Thermal Analysis

The technique of DTA and the apparatus used in the Physical Chemistry Group's Thermoanalytical laboratory are described in Mines Branch Technical Bulletin TB 92<sup>(2)</sup>. Briefly, in the current investigation, the samples were heated in a palladium sample holder employing  $\alpha$ -alumina as the reference material at a heating rate of 12 deg C per minute. Pt vs Pt:13% Rh thermocouples were used to measure the sample and differential temperatures while the differential sensitivity used throughout the tests was 10 micro-volts per inch of chart. Thermograms were obtained from all six samples while they were being heated to a temperature of 1050°C in each of three different atmospheres: (a) static air, (b) flowing N<sub>2</sub>, and (c) flowing CO<sub>2</sub>.

### (B) Thermogravimetric Analysis

The thermogravimetric analyses were conducted in a Stanton Recording Thermobalance. The heating rate was approximately 6 deg C per minute and, as in the DTA tests, thermograms were obtained on the six samples while they were being heated to a temperature of 1050°C in each of the atmospheres: static air, flushing N<sub>2</sub>, and flushing CO<sub>2</sub>. The initial and final sample-weights were determined independently on an analytical balance, as a check on the total net weight change, while the

various stages of weight change during the tests were derived from the thermobalance charts.

### EXPERIMENTAL RESULTS AND DISCUSSION

The DTA thermograms of all six samples showed the endothermic quartz  $\alpha \rightarrow \beta$  crystal-inversion peak between 570°C and 590°C, and from the size of the peaks, it was apparent that quartz was the major component of four of the six samples, one of the major components of another of the samples, and a minor component of the remaining sample.

The presence of hematite in all six samples was indicated by the endothermic transition from the paramagnetic to the antiferromagnetic state at the Néel temperature (approximately 690°C). An estimate of the amount of hematite in the samples, again based on the size of the peaks, indicated that it was a major component in two of the samples and a small to very small minor component of the other four samples.

It is recognized, of course, that the basic energies involved in the various reactions occurring in the samples are not likely to be the same and, therefore, a direct comparison of the absolute size of the peaks on a thermogram will not necessarily reflect the relative abundance of the constituents giving rise to the reactions. Hence, it is pointed out that the estimates of the relative abundance of the components in these samples are based, not only on the size of the peaks, but also on a considerable background of experience obtained from studying the DTA curves produced in previous work on standard samples or on relatively pure specimens of the various substances found in this investigation.

The DTA curves of four of the samples, when heated in an air atmosphere, showed small exotherms which peaked in the range 830°C to 835°C. These exotherms did not appear on the thermograms of the same samples when heated in either a flowing nitrogen or in a flowing carbon dioxide atmosphere. It is, therefore, considered that the presence of

small to very small minor amounts of magnetite in these samples is indicated because natural mineral magnetite is known to oxidize to hematite when heated above 750°C in an oxidizing atmosphere, as opposed to synthetically prepared  $\text{Fe}_3\text{O}_4$  which oxidizes to  $\text{Fe}_2\text{O}_3$  at about 200°C under the same conditions. The exothermic transition of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) to hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) which occurs at approximately 500°C, did not show on the thermal curves of any of the samples.

The presence of a hydrated iron oxide in a sample is made evident in its DTA thermogram by the endothermic reaction caused by the expulsion of the water molecule or molecules from the compound. This may take place in one or more stages and may result in a single endothermic peak or, alternatively, in an endotherm that may be resolved or partly resolved into more than one peak, in which case the endotherm will either have two discrete peaks or one main peak with a shoulder on one side. The temperature at which the peak or peaks will occur varies with the particular hydrous iron oxide concerned and also with the conditions under which the DTA test is conducted, and particularly with the rate of temperature increase during the test. In the case of limonite, (approximately  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) the evolution of the combined water produces an endotherm that peaks in the temperature range 300° to 375°C, whereas, in the case of goethite ( $\alpha\text{-FeO} \cdot \text{OH}$ ), the peaking usually occurs in the temperature range 375°C to 450°C, although, with some specimens, it has been found to be somewhat lower than this and, hence, in the same range as that of limonite. Lepidocrocite ( $\gamma\text{-FeO} \cdot \text{OH}$ ) also has this endotherm in the same temperature range as goethite, (i. e., 375°C-450°C), but, in this case, it is followed almost immediately by an exotherm that peaks at about 500°C and is caused by the transition of the  $\gamma\text{-Fe}_2\text{O}_3$  formed by the reaction to  $\alpha\text{-Fe}_2\text{O}_3$ . This exotherm, therefore, provides a basis for distinguishing goethite from lepidocrocite.

All of the samples investigated showed an endotherm on their DTA curves that peaked in the temperature range 300°C-365°C. In three cases, viz., Samples 1, 3, and 6, the endotherm formed a single peak, but,

in the other three Samples 2, 4, and 5, the endothermic peak exhibited a shoulder on the low-temperature side. In view of the temperature range in which this reaction occurs in all six samples and in the light of the results of previous work done on similar Wabush iron ore samples in which the iron minerals present were identified mineralogically as hematite and limonite and which produced thermograms similar to those of the samples in the present investigation, it is considered most probable that the hydrated iron oxide present is limonite and, furthermore, because none of the samples showed an exothermic peak following this endotherm, the presence of lepidocrocite as a constituent may be ruled out. The presence of a very small amount of adsorbed moisture in the samples was indicated by a broad, shallow, endothermic flexure on the DTA curves between 100°C and 250°C.

Siderite ( $\text{FeCO}_3$ ) decomposes with the evolution of  $\text{CO}_2$  in the temperature range 500°C-600°C. In an air atmosphere, this endothermic reaction is followed immediately by a strong exotherm caused by the oxidation of the  $\text{FeO}$  formed. If a flowing  $\text{CO}_2$  atmosphere is used instead of an air atmosphere during a DTA run on a carbonate mineral, the decomposition will be somewhat delayed by the increased  $\text{CO}_2$  pressure and, as a result, the endotherm that is produced will form a much sharper peak with a higher amplitude and narrower base, usually at a somewhat higher peak temperature. By this means, it is often possible to detect the presence of a very small amount of a carbonate mineral in a sample. However, in this investigation, no peaks characteristic of the mineral siderite were detected on the DTA thermograms with any of the six samples, whether examined in an air or in a  $\text{CO}_2$  atmosphere; it is, therefore, concluded that, if siderite is present in any of the samples, it is in no greater than a trace quantity only.

Thermogravimetric analysis of the samples showed that the total weight losses during the heating program varied between a minimum of 0.6% and a maximum of 1.9%, based on the starting weight of the samples. The weight losses could, in general, be separated into three stages,



corresponding in temperature range to those indicated by the DTA thermograms. These included firstly, a slight loss occurring from R. T. to about 200°C, secondly, the major loss in all samples, occurring in the temperature range of the DTA peaks, caused by the decomposition of the hydrous iron oxide and thirdly, a final slight continuing loss to the end of the run.

Although the completion of the second or major stage in all cases was quite distinct on the TGA curves, the beginning of this stage and the end of the first or adsorbed-water-loss stage was not. The amount of adsorbed water in some of the samples, as taken from the charts in those cases that could be approximately determined from the change in the slope of the TGA curves between the first two stages, averaged about 0.1%; this figure was assumed to hold also for those cases that could not be so determined. Hence, as the weight losses involved are quite small, thus increasing the degree of uncertainty, the amount of limonite calculated to be present in the samples, based on these weight losses, must be regarded at best as semi-quantitative.

The results of the tests, as discussed in the foregoing, are summarized in Table 2.

Figures 1 and 2 are reproductions of typical DTA thermograms that were obtained during the tests.

Figures 3 and 4 are reproductions of typical TGA thermograms that were obtained during the tests.

TABLE 2

Results of Thermoanalytical Tests on Wabush Iron Ore Samples

Sample Constituent	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Quartz ( $\text{SiO}_2$ )	Major	Major	Major	Minor	Major	Major
Limonite (approx. $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) (approx. quantity given in brackets)	Small minor (3%)	Small minor (5%)	Small minor (5%)	Small minor (2%)	Minor (9%)	Small minor (3%)
Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ )	Small minor	Small minor	Small minor	Major	Major	Very small minor
Magnetite ( $\text{Fe}_3\text{O}_4$ )	-	Very small minor	Small minor	Small minor	Small minor	-
Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ )	-	-	-	-	-	-
Goethite ( $\alpha\text{-FeO} \cdot \text{OH}$ )	-	-	-	-	-	-
Lepidocrocite ( $\gamma\text{-FeO} \cdot \text{OH}$ )	-	-	-	-	-	-
Siderite ( $\text{FeCO}_3$ )	-	-	-	-	-	-

REFERENCES

1. R.G. Pinard, "Separation and Mineralogical Investigation of a Fine-Grained Table Tailing of Wabush Iron Ore", Mineral Sciences Division Internal Report MS 72-3, February 16, 1972.
2. R.H. Lake, "The Construction, Operation and Performance of an Equipment for Differential Thermal Analysis", Mines Branch Technical Bulletin TB 92, August, 1967.

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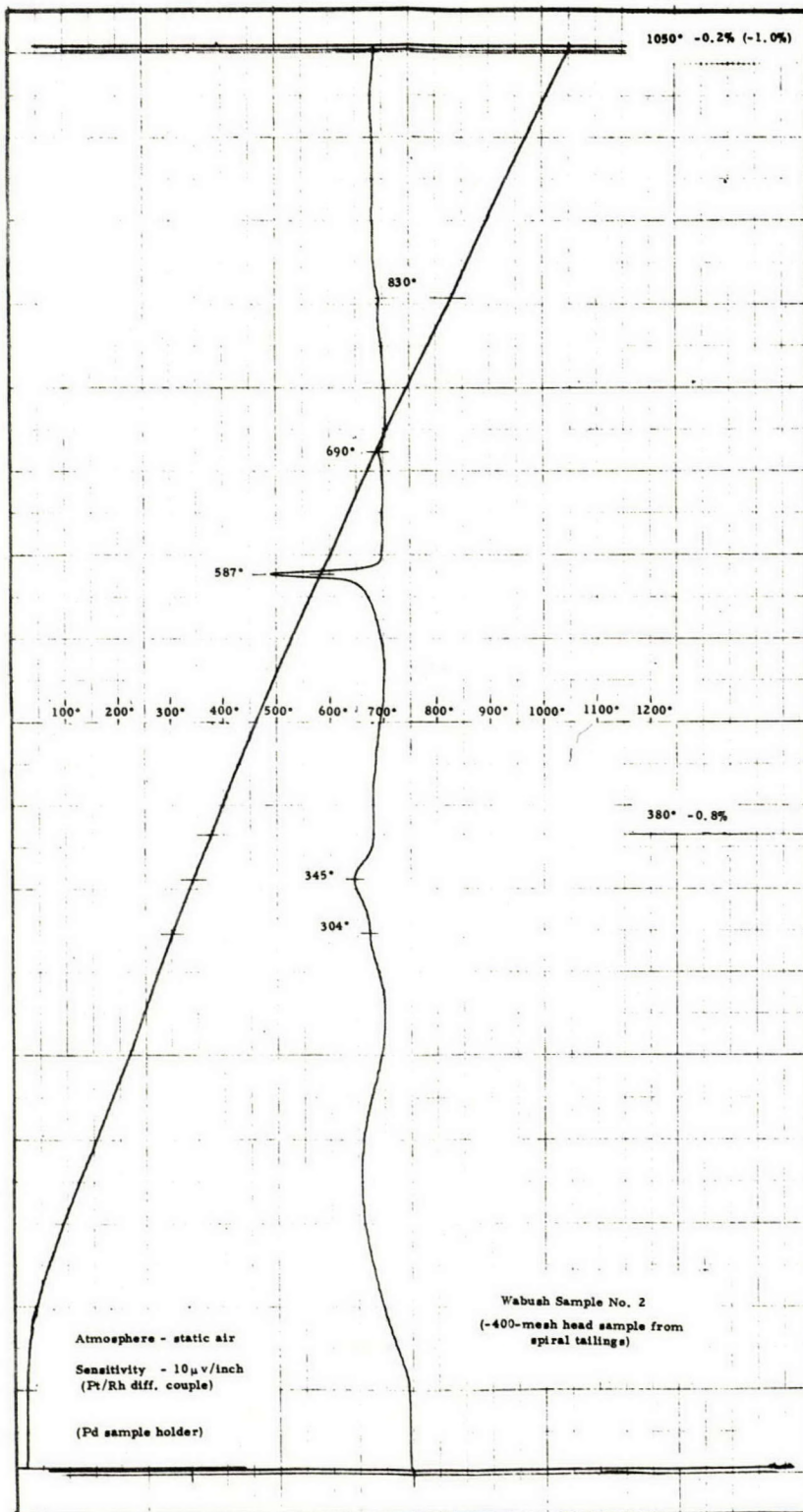


Figure 1. DTA Thermogram of Sample No. 2 (air atmosphere)

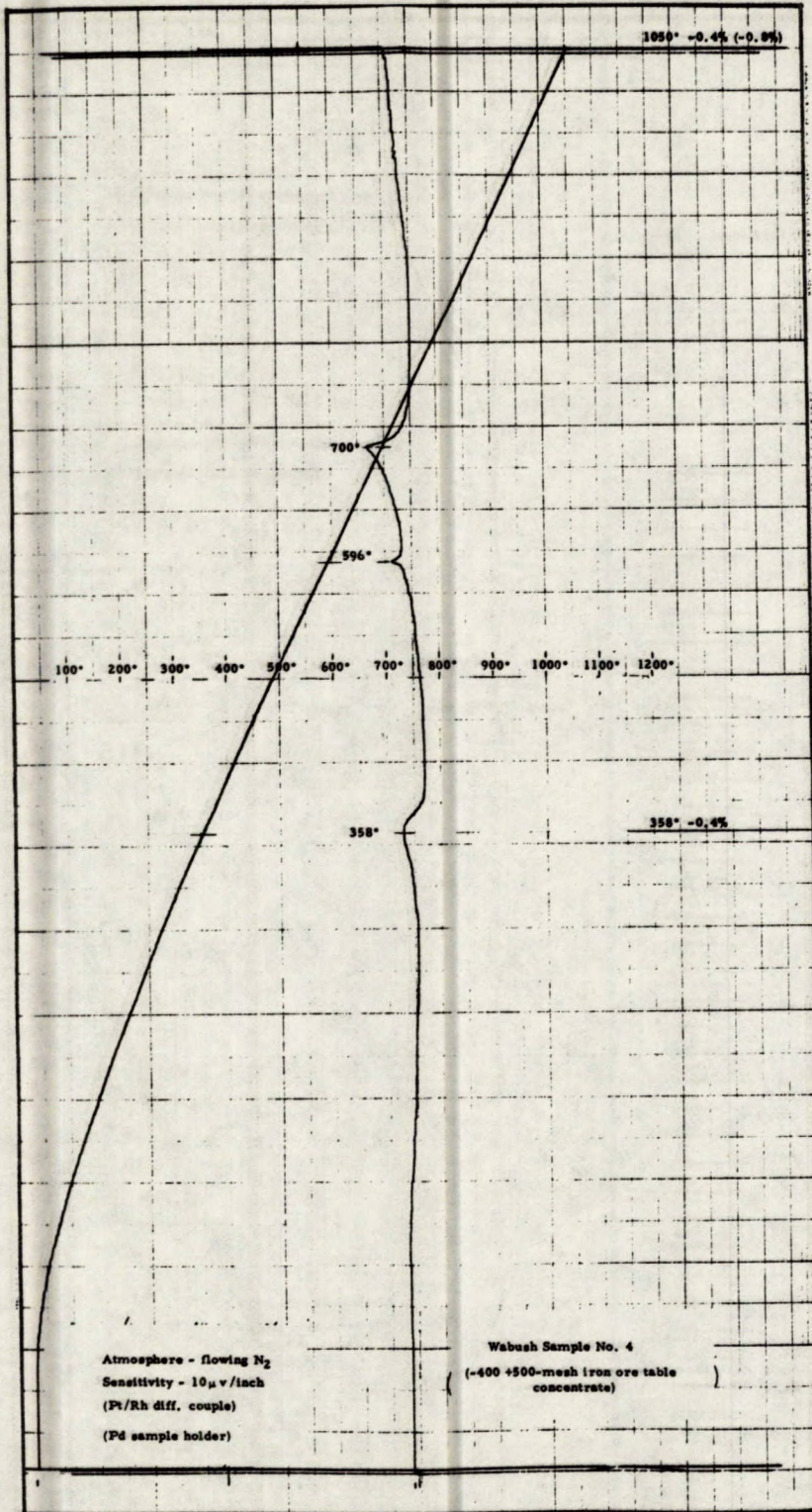


Figure 2. ETA Thermogram of Sample No. 4 (nitrogen atmosphere)

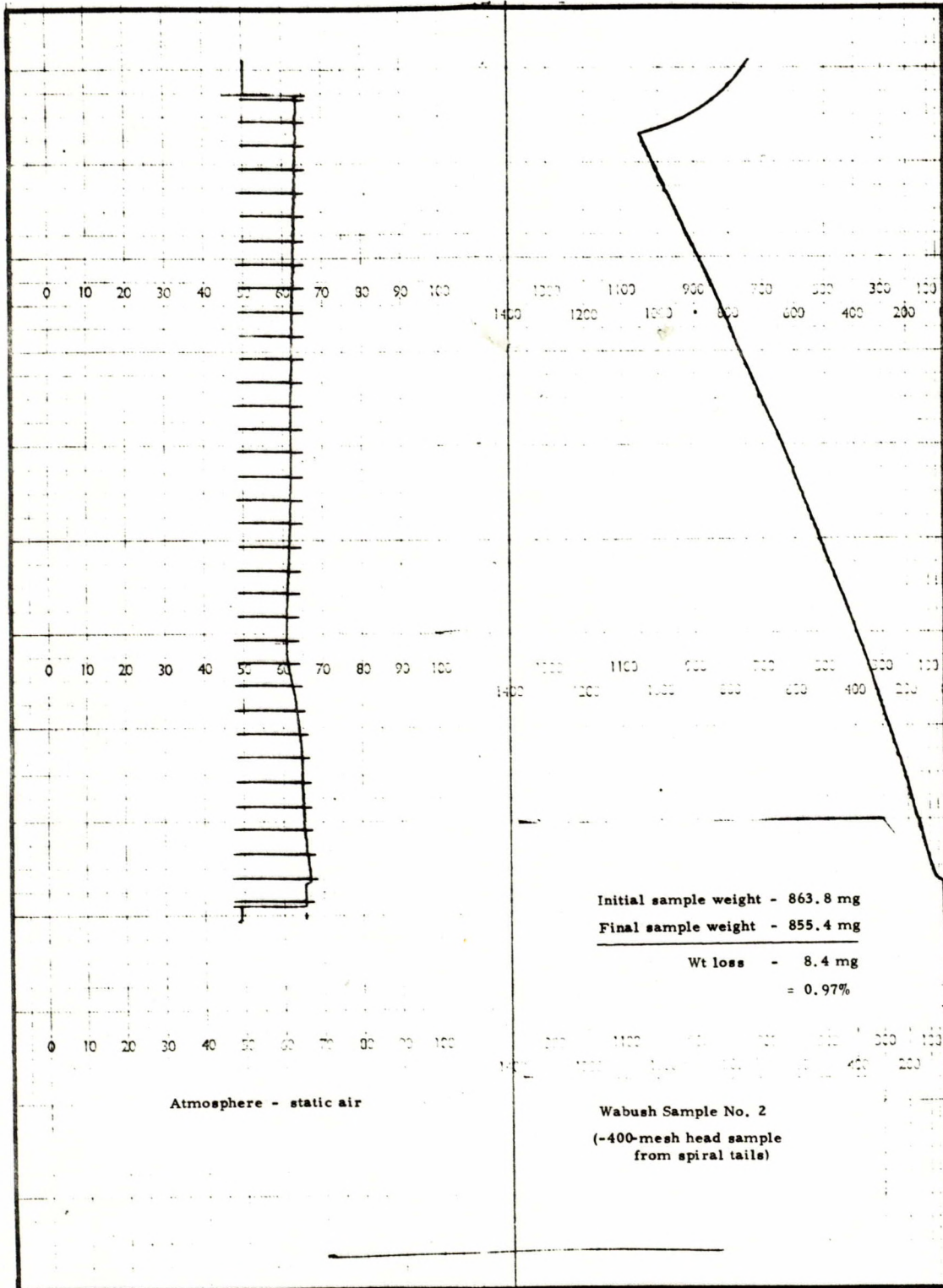


Figure 3. TGA Thermogram of Sample No. 2 (air atmosphere)

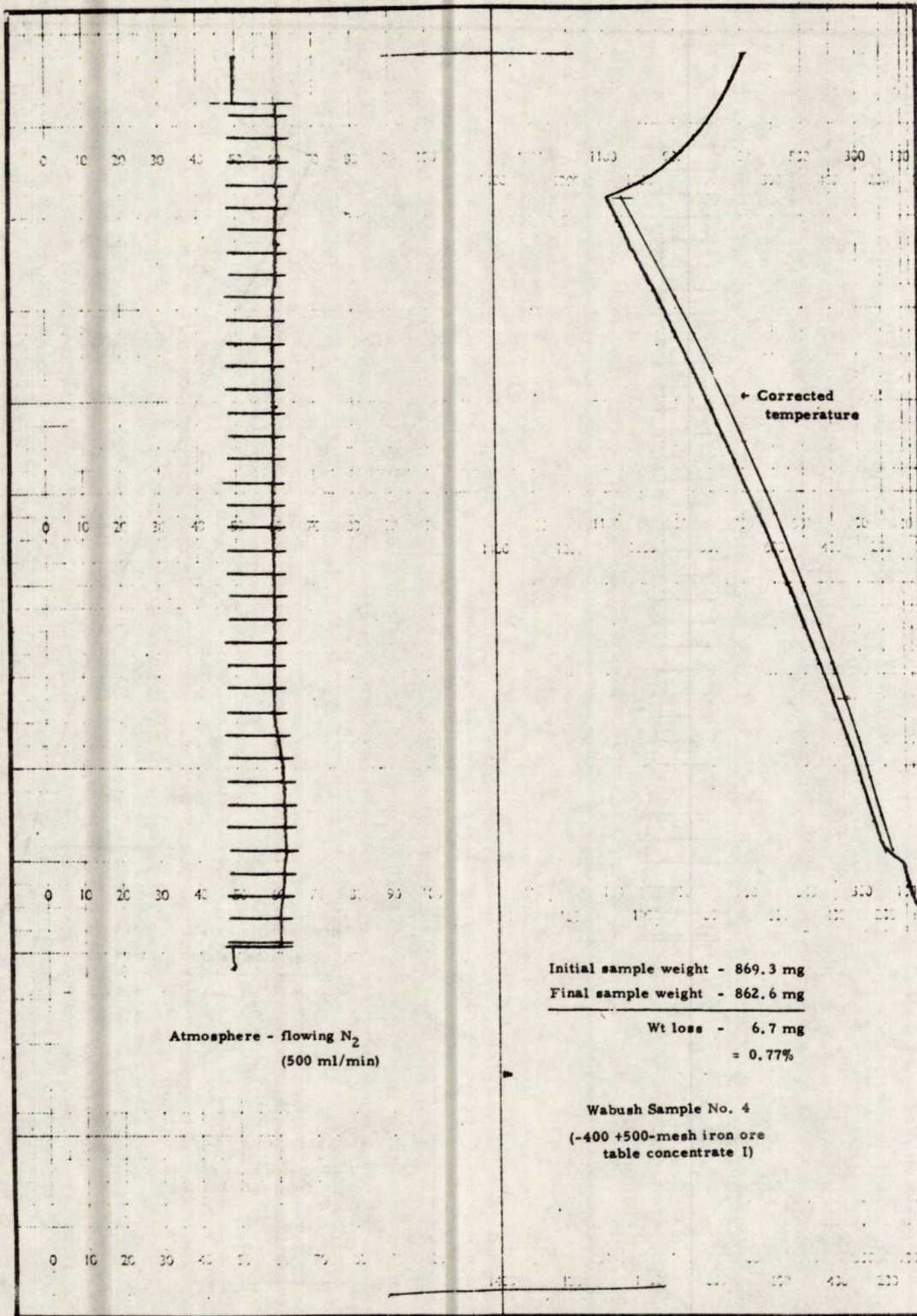


Figure 4. TGA Thermogram of Sample No. 4 (nitrogen atmosphere)