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IR 71-41 June 23, 1971

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MINERAL SCIENCES DIVISION

Mines Branch Investigation Report IR 71-41

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SUMMARY

Thermogravimetry, differential thermal analysis, and X-ray diffraction techniques were employed to study the thermal decomposition of freeze-dried $MnSO_4$, $ZnSO_4$, $FeNH_4(SO_4)_2$ and $FeSO_4.(NH_4)_2SO_4$. Freeze-dried mixtures of $MnSO_4$ and/or $ZnSO_4$ with $FeNH_4(SO_4)_2$ or $FeSO_4.(NH_4)_2SO_4$ were also examined. Decomposition temperatures and proposed decomposition mechanisms are given.

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INTRODUCTION

Many applications of soft-ferrite ceramic components require very narrow tolerances in the properties of the ferrite. Since the properties of soft ferrites are critically dependent on their composition, a strict control of stoichiometry is necessary in order to ensure chemically reproducible products. The analytical chemistry of these ferrites, particularly the mixed ferrite such as Mn-Zn ferrite, is rather complicated. It involves the separation of very closely related elements. Since the accuracy demanded is generally very high, these analyses become both difficult and expensive to perform. Furthermore, since the chemical analyses will give information only on the bulk composition, they yield no information on the homogeneity of the materials. It is, therefore, easier to control the composition by using well-analysed raw materials in the preparation. The conventional method of preparation relies on thermal diffusion in the solid state to homogenize the reaction products down to the grain level. There are many factors that can easily upset both the metals stoichiometry of the product and its degree of homogeneity. For example, a slight change in the milling conditions can alter the Fe/(Mn + Zn) ratio, due to the introduction of more or less additional iron from the milling equipment. Similarly, a slight change in the particle size of the raw materials will require a corresponding change in the calcination cycle to achieve an equivalent degree of homogeneity; this will result in a change of the particle characteristics of the reacted powder.

Various methods of preparation have been developed in order to solve these difficulties. Such methods include the co-precipitation technique, the spray-drying method, etc., which have been reported to have had a certain degree of success for certain systems. In the present work, a freeze-drying method of preparation was studied for the system of Mn-Zn

ferrite. The mechanism of the reactions leading to the formation of the ferrite compound was studied by XRD, TGA and DTA techniques.

EXPERIMENTAL PROCEDURES

1. Sample Preparation

Reagent grades of $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $FeNH_4(SO_4)_2 \cdot 12H_2O$ and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ were dissolved in distilled water, acidified with dilute H_2SO_4, filtered, and the resulting solutions were assayed chemically(1). These solutions were blended volumetrically to give mixtures that would yield a range of manganese-zinc ferrite compositions. These compositions are given in Table I.

The mixtures were sprayed in the form of fine mists into a bath of liquid nitrogen. In this way, the individual droplets were frozen instantly, thus minimizing the possibility of segregation of the components. The samples were then subjected to freeze-drying. This method of sample preparation has been described by Mirkovich and Wheat(2).

The samples designated A, B and C in Table I were analysed spectrographically for their impurity content. The results are given in Table II.

2. TGA, DTA and XRD Examinations

(NOTE: TGA = thermogravimetric analysis; DTA = differential thermal analysis; XRD = X-ray diffraction)

The TGA examinations were conducted in a static-air atmosphere, using a Stanton Automatic Recording Thermobalance. A platinum crucible was used as container. The sample was heated to 1050°C or to 1100°C at a rate of 360 deg C per hour. No further weight changes occurred above this temperature. A few runs were also made in a flowing-nitrogen atmosphere.

The DTA examinations were conducted in a static-air atmosphere at a heating rate of 12 deg C per minute. The standard reference material used was α-alumina. The sample was held in a palladium holder. The

TABLE I

Nominal Composition of Samples (mole % cations)

Sample Designation	Mn^{++}	Zn^{++}	$(Fe^{+++})_2$	$(Fe^{++})_2$
A	100.0	-	-	-
B	-	100.0	-	-
C	-	-	100.0	-
D	-	-	-	100.0
1	50.0	-	50.0	-
2	-	50.0	50.0	-
3	26.4	23.6	50.0	-
4	47.5	-	52.5	-
5	-	47.5	52.5	-
6	25.5	22.0	52.5	-
7	50.0	-	-	50.0
8	-	50.0	-	50.0
9	26.4	23.6	-	50.0
10	47.5	-	-	52.5
11	-	47.5	-	52.5
12	25.5	22.0	-	52.5

TABLE II

Semi-Quantitative Spectrographic Analyses of Freeze-Dried Samples (Wt %)*

Elements	Sample "A" (Manganese Sulphate)	Sample "B" (Zinc Sulphate)	Sample "C" (Ferric Ammonium Sulphate)
Ba	N. D.	N. D.	N. D.
Mn	P. C.	N. D.	N. D.
Sb	N. D.	N. D.	N. D.
As	N. D.	N. D.	N. D.
Mg	N. D.	N. D.	N. D.
Mo	0. 04	N. D.	N. D.
W	N. D.	N. D.	N. D.
Pb	N. D.	N. D.	N. D.
Sn	N. D.	N. D.	N. D.
Cr	N. D.	N. D.	N. D.
Si	N. D.	N. D.	N. D.
Nb	N. D.	N. D.	N. D.
Ta	N. D.	N. D.	N. D.
Fe	N. D.	N. D.	P. C.
Bi	N. D.	N. D.	N. D.
Al	N. D.	N. D.	N. D.
V	N. D.	N. D.	N. D.
Ca	N. D.	N. D.	N. D.
In	N. D.	N. D.	N. D.
Zr	0. 02	N. D.	N. D.
Cu	0. 006	N. D.	N. D.
Ag	N. D.	N. D.	N. D.
Na	N. D.	N. D.	N. D.
Zn	N. D.	P. C.	N. D.
Ti	N. D.	N. D.	N. D.
Ni	N. D.	N. D.	N. D.
Co	N. D.	N. D.	N. D.
Sr	N. D.	N. D.	N. D.

*N. D. - Non detectable; P. C. . Principal constituent.
Analysis by D. P. Palombo, see Mineral Sciences Division Internal Report MS-AC-69-650.

thermocouples used were Pt vs Pt: 13% Rh for both sample and differential temperature measurements. The differential EMF and the sample-holder temperature were simultaneously recorded on a two-pen recorder, the former after amplification and the latter directly. In order to elucidate particular points, some runs were made with a heating rate of 6 deg C per minute and/or a flowing-argon atmosphere.

X-ray powder diffraction patterns of the samples that had been examined by TGA and DTA, were prepared in order to identify the products of the thermal decompositions. The films were obtained with a 114.6-mm-diameter Debye-Scherrer camera, using filtered CoK_{α} radiation.

EXPERIMENTAL RESULTS AND DISCUSSION

The XRD examination of the freeze-dried products revealed that they contained very little crystalline material and nothing that could be identified. The static-air DTA and TGA thermograms of Samples A, B, C, D, 3 and 9 are reproduced in Figures 1 to 6, respectively.

The TGA of Sample A showed that the starting material was approximately the mono-hydrate, $MnSO_4.H_2O$. The water was lost by the time a temperature of 265°C was reached. There was no further weight loss until 800°C, after which there was a steady loss until a temperature of 980°C was reached. This loss is associated with the decomposition of $MnSO_4$. XRD examination of the product that had been heated to 1100°C showed some evidence of oxidation having occurred, as the major phase was Mn_3O_4 (minor = Mn_2O_3). The weight-loss figures supported this conclusion.

Sample B contained approximately 1 mole of H_2O per mole of $ZnSO_4$. In this case, the water was evolved by the time a temperature of 300°C was reached with no further change until 680°C.

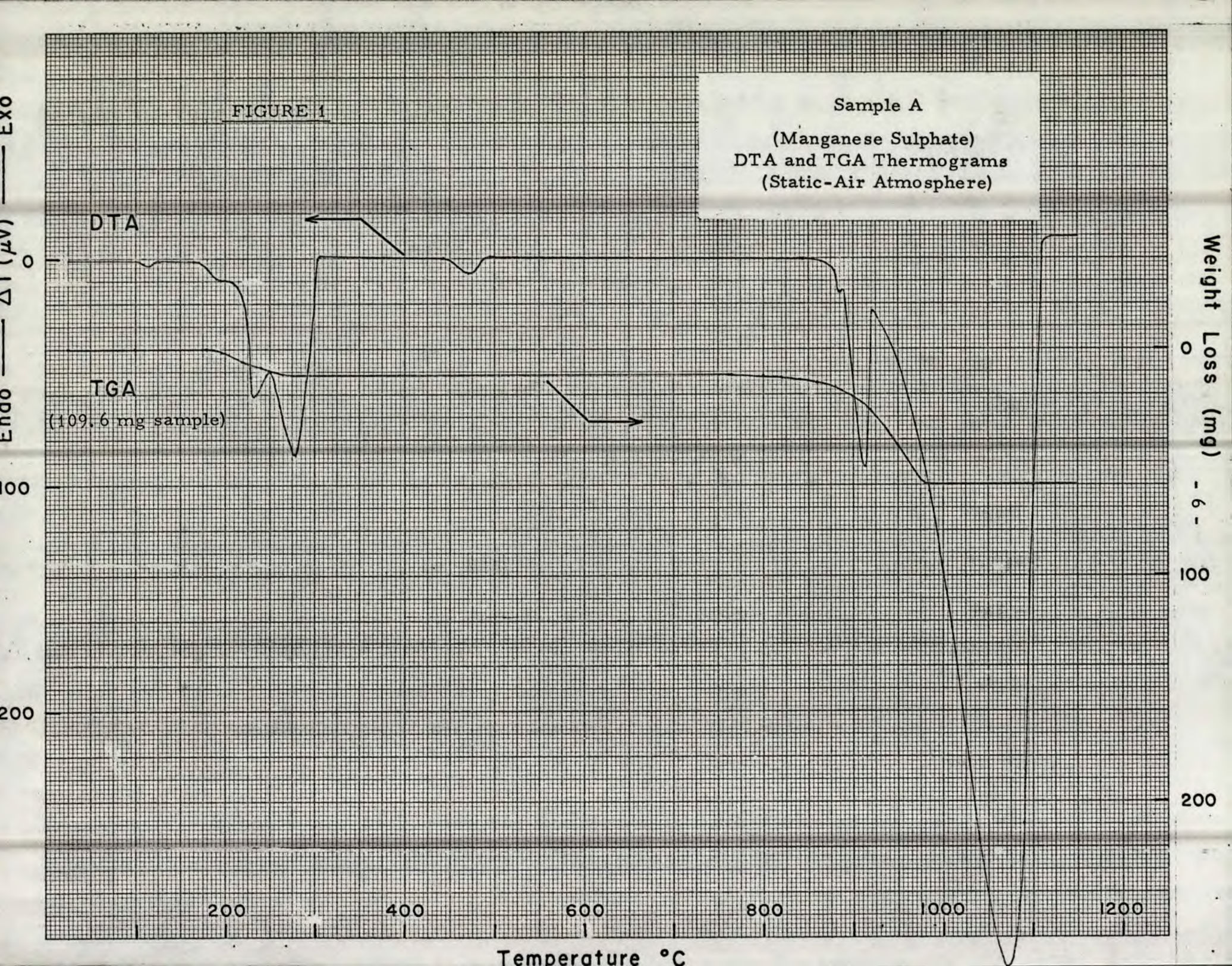


FIGURE 1
Sample A
(Manganese Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
DTA
TGA
(109.6 mg sample)
Endo ——— ΔT (μV) ——— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

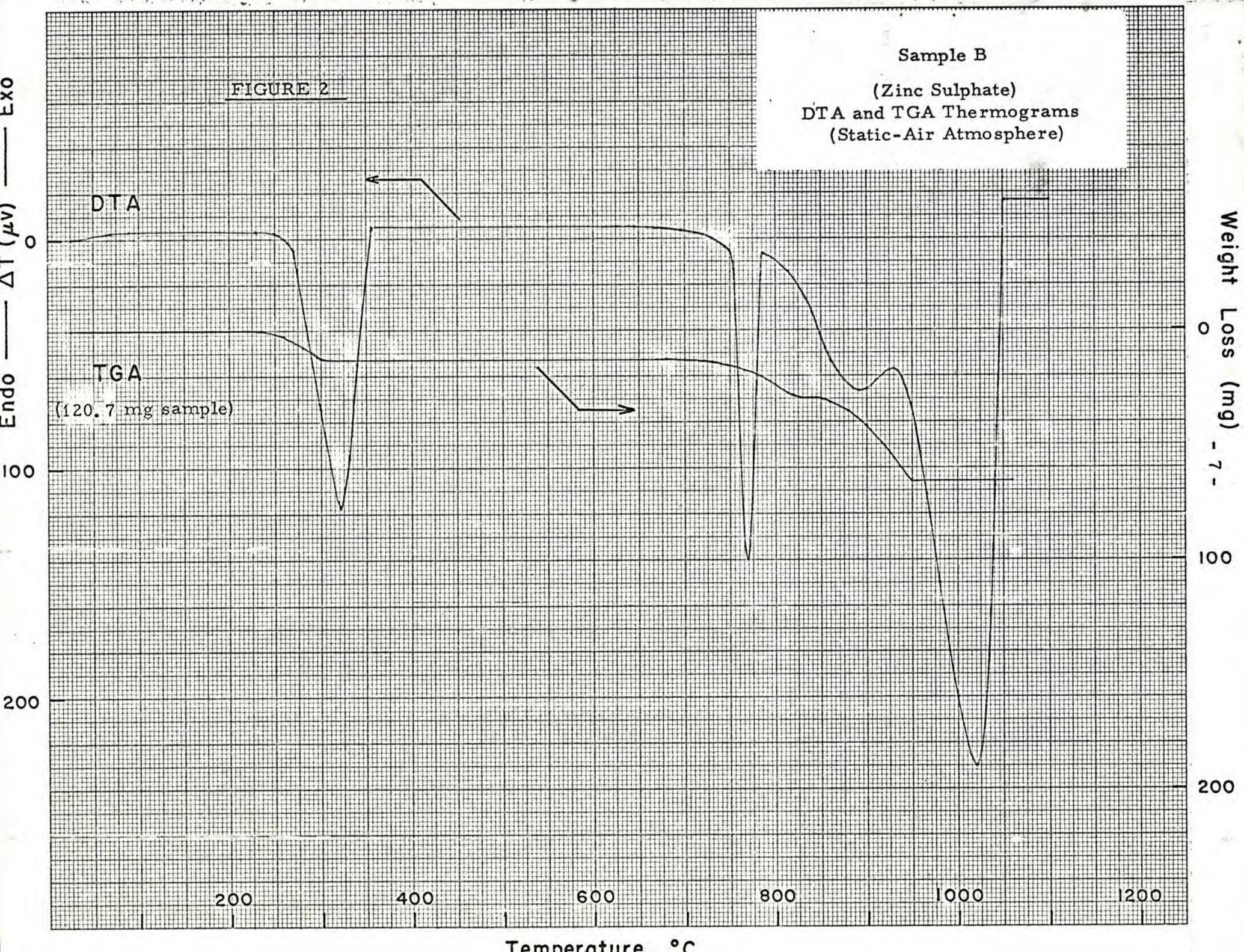
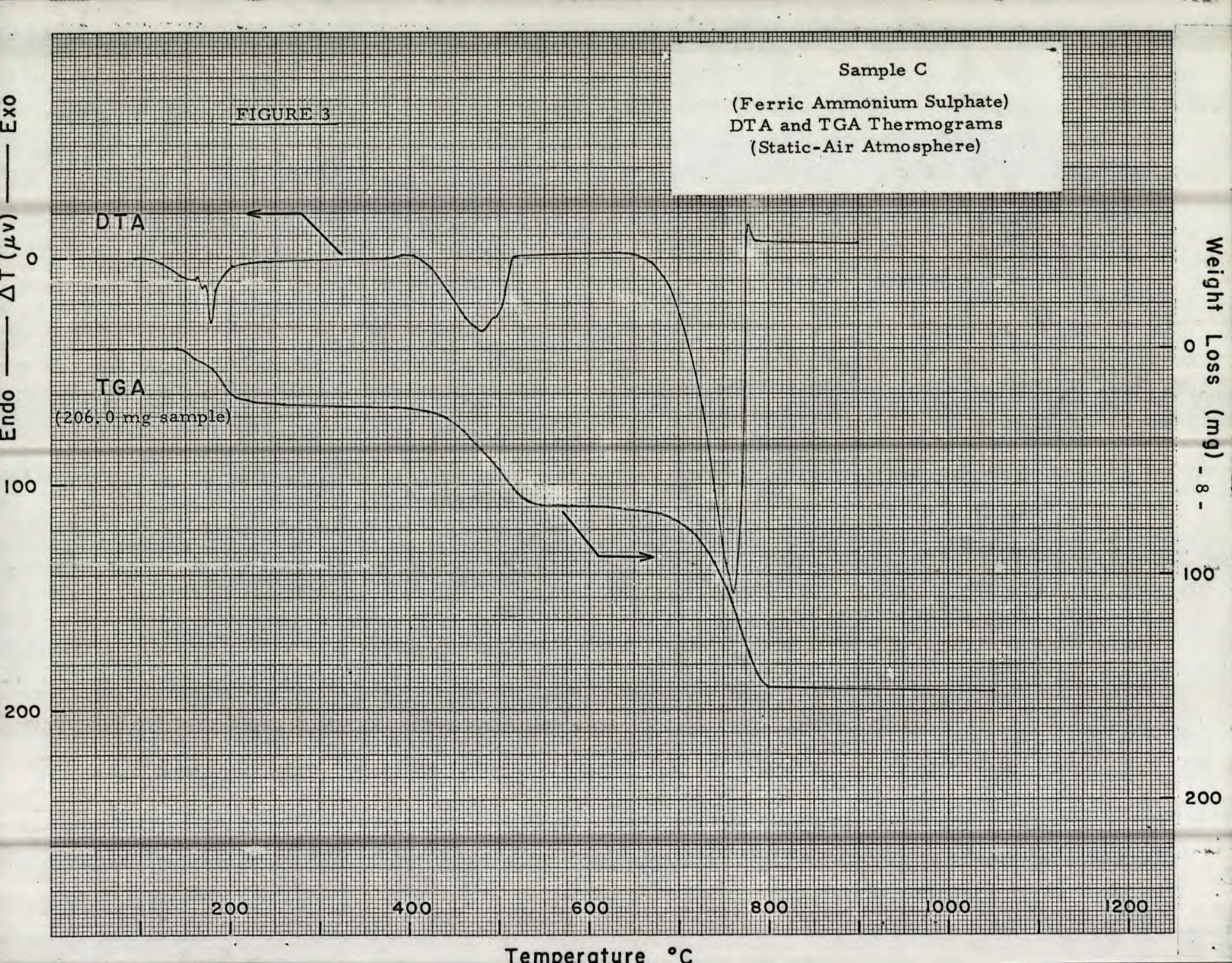

Sample B
(Zinc Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
DTA
TGA
(120.7 mg sample)
Endo —— ΔT (μv) —— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

FIGURE 2


Sample C
(Ferric Ammonium Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
FIGURE 3
DTA
TGA
(206.0 mg sample)
Endo —— ΔT (μv) —— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

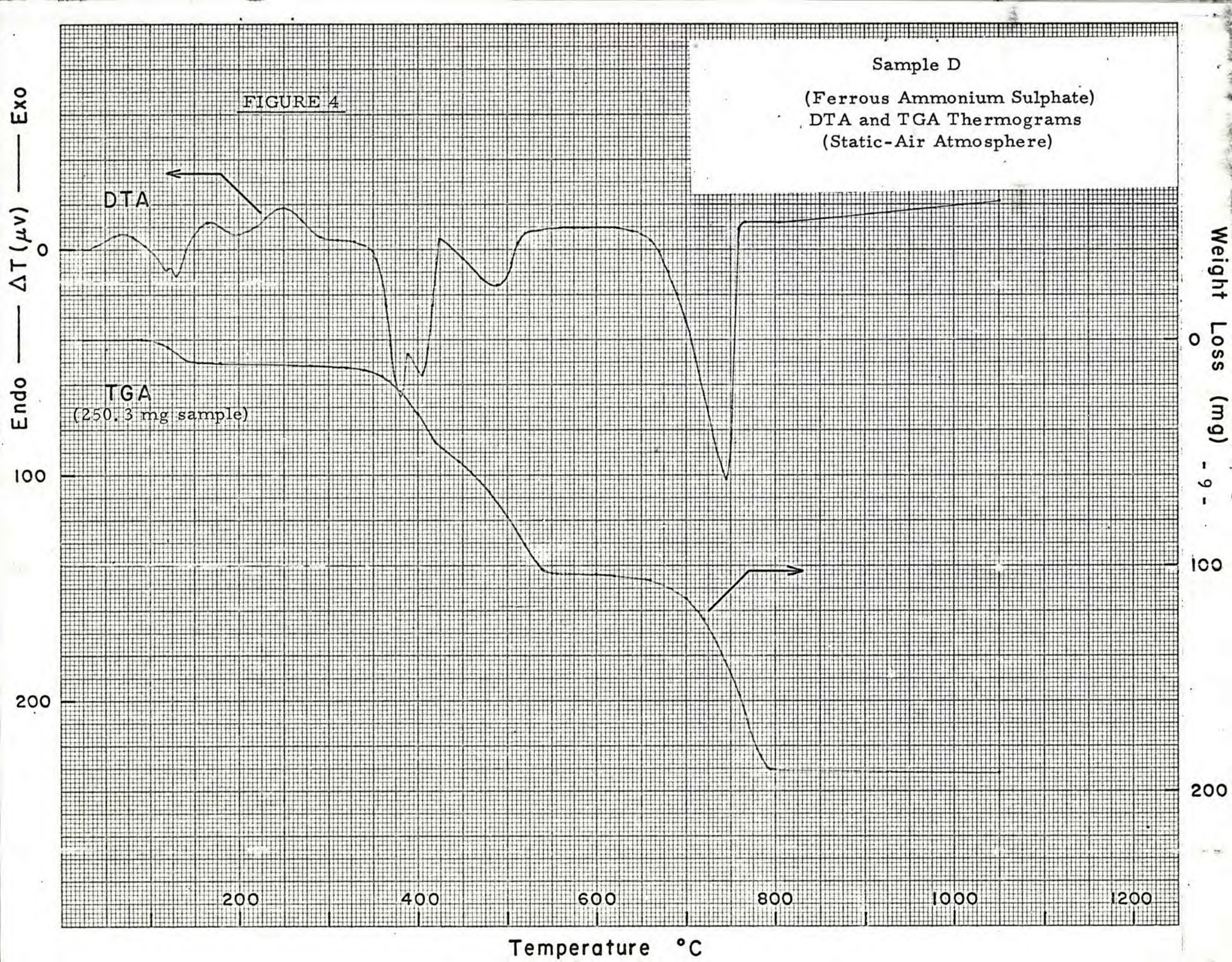

Sample D
(Ferrous Ammonium Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
DTA
TGA
(250.3 mg sample)
Endo —— ΔT (μv) —— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

FIGURE 4

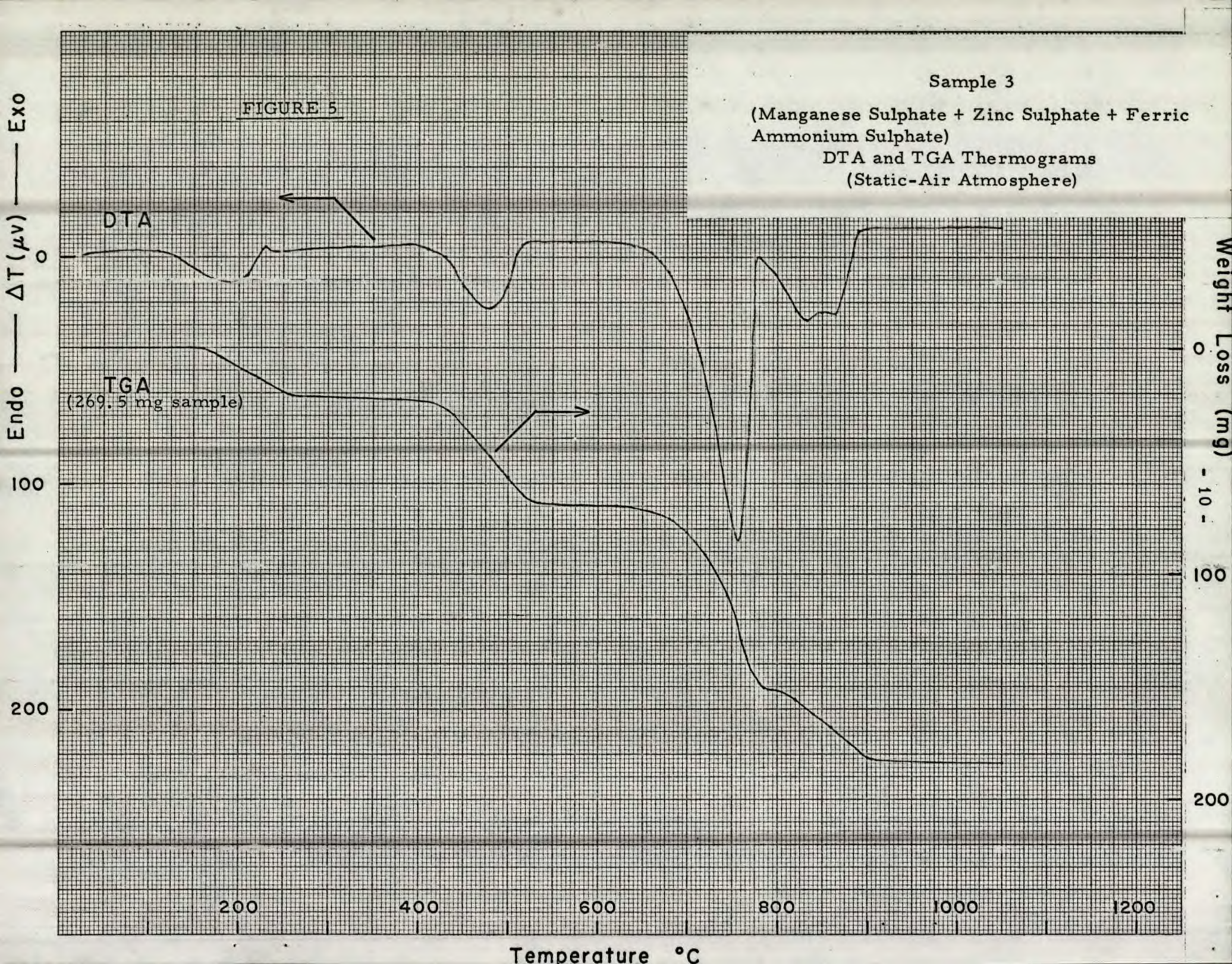


FIGURE 5
Sample 3
(Manganese Sulphate + Zinc Sulphate + Ferric Ammonium Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
DTA
TGA
(269.5 mg sample)
Endo —— ΔT (μv) —— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

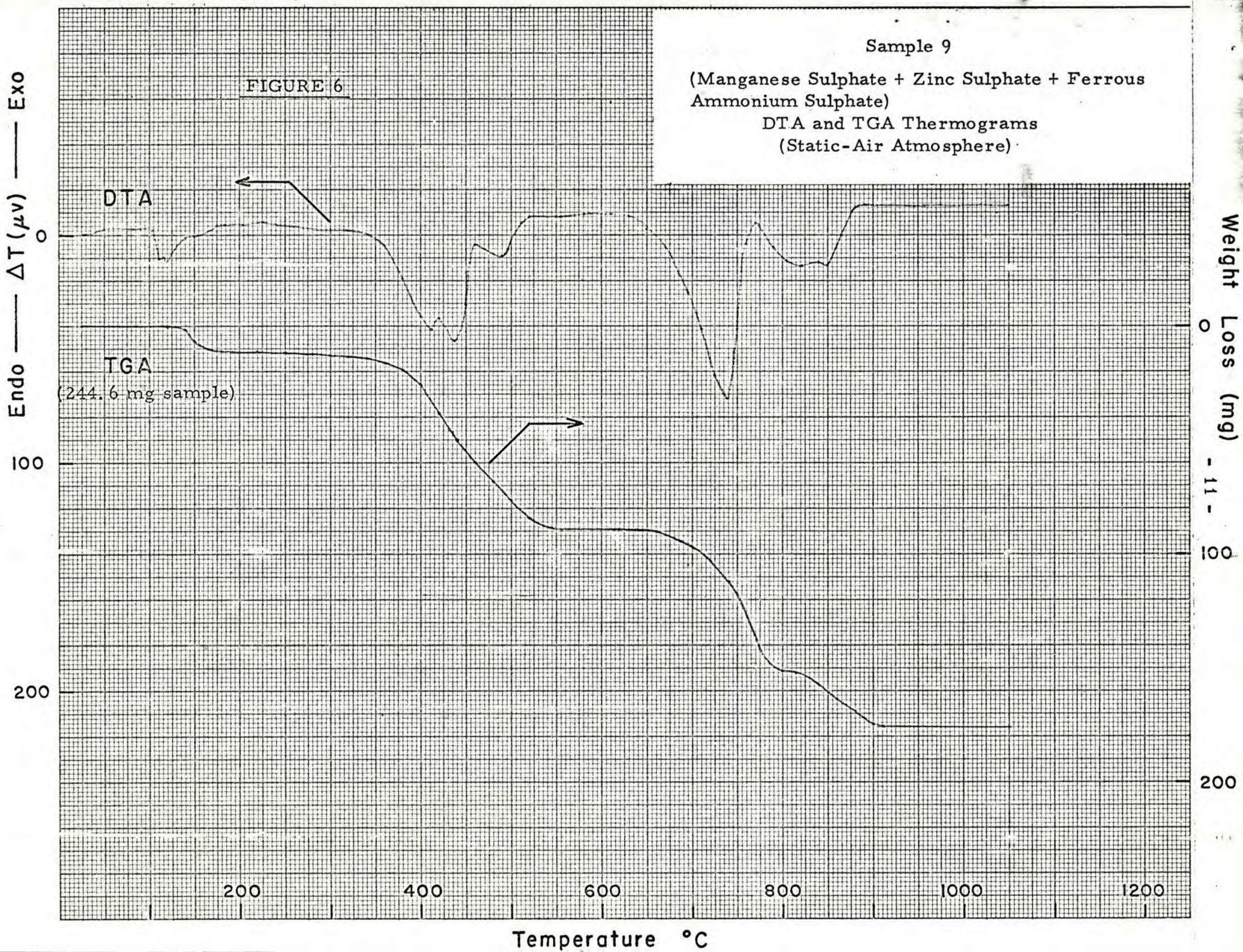


FIGURE 6
Sample 9
(Manganese Sulphate + Zinc Sulphate + Ferrous Ammonium Sulphate)
DTA and TGA Thermograms
(Static-Air Atmosphere)
DTA
TGA
(244.6 mg sample)
Endo —— ΔT (μv) —— Exo
0
100
200
Weight Loss (mg)
0
100
200
200
400
600
800
1000
1200
Temperature °C

At this temperature, a two-stage weight loss was initiated that was complete at 950°C. The weight-loss curve showed an inflection point at 840°C. The relative weight-loss figures indicated that the first stage was due to the decomposition to 2 $ZnSO_4 . ZnO$, while the second stage was caused by the complete decomposition to ZnO. The former product is consistent with that reported by other workers(3), while the latter was confirmed by XRD.

Sample C had the composition of approximately $Fe\ NH_4(SO_4)_2 . 2H_2O$. The water was lost by 300°C. This loss was followed by a further weight loss occurring from 380°C to 540°C; this was consistent with the decomposition of $(NH_4)_2SO_4$. There was an additional loss from 620°C to 800°C, due to the decomposition of $Fe_2(SO_4)_3$, yielding Fe_2O_3. These observations are consistent with the DTA curve and with the XRD examination of the final product.

Sample D had approximately the composition $Fe\ SO_4 . (NH_4)_2SO_4 . 3H_2O$. The initial weight loss, which was complete by about 160°C, accounted for less than half of the water. A second loss, occurring from 280°C to 550°C, was apparently the result of three processes:

(i) the loss of the remaining water;
(ii) the decomposition of $(NH_4)_2SO_4$; and
(iii) the oxidation of Fe^{+2} to Fe^{+3}.

The oxidation of $FeSO_4$ was confirmed by DTA. When the sample was heated in air, only a small endothermic peak was observed; this would be the result of the off-setting action of the exothermic oxidation process against the endothermic sulphate-decomposition reaction. However, when the sample was heated in a flowing-argon atmosphere, a large endothermic peak only was observed, due to the decomposition of $(NH_4)_2SO_4$; under these conditions, the oxidation reaction was suppressed. There was an additional weight loss from 550°C to 800°C which is consistent with the decomposition of $Fe_2(SO_4)_3$. Fe_2O_3 was found by XRD to be the final product.

The thermograms of Samples 1 to 12 showed that the components of these samples (A and/or B with C or D) behaved almost independently. This is indicated by Figures 5 and 6. Decomposition temperatures were somewhat lower and the final products generally consisted of the corresponding spinel ferrites. Sample 1 and Sample 7 did not yield manganese ferrite but, rather, a mixture of Mn_2O_3 and Fe_2O_3. (Samples 4 and 10 were not examined by XRD but would, presumably, have given the same result). A TGA run was made for Sample 1 in a flowing-nitrogen atmosphere; the decomposition temperatures were again lower and the final product was $MnFe_2O_4$. An excellent $ZnFe_2O_4$ XRD powder pattern, free from foreign lines, was obtained from Sample 8. The thermograms for Samples 3, 6, 9 and 12 showed that the $MnSO_4$ and $ZnSO_4$ decomposed together, although two peaks were observed by DTA. It is not unusual for the DTA technique to be more sensitive, in resolving reactions occurring at closely spaced temperatures, than is the thermogravimetric technique.

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