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RDTR No. 36
25 March 1964

INVESTIGATION OF
MK 25 MOD 2 STARTER COMPOSITION

U. S. NAVAL AMMUNITION DEPOT
Crane, Indiana

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SIGNED S. M. Fasig
S. M. FASIG, Director, Research and Development Department

TABLE OF CONTENTS

RDTR No. 36
25 March 1964

ABSTRACT

A study is made on various chemical and physical characteristics of the Mk 25 Mod 2 Starter Composition, which is an oxygen deficient silicon - lead dioxide - cupric oxide system. A scheme for chemical analysis, already provided in RDTR No. 27, is reviewed. Physical phase changes and chemical reaction mechanism of the components, and of the mixture as a whole, are explored by differential thermal analysis and thermogravimetric analysis. The principal chemical reactions are considered and the theoretical thermodynamic values compared with experimental values. Behavior characteristics, such as sensitivity, stability, heat of reaction, ignition point, and other available information are included in a Pyrotechnic Data Collection Sheet.

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1. INTROUCUCTION

a. The Chemical Laboratory Branch has been given the task of compiling data sheets on R & D pyrotechnic compositions. The accumulation of this data necessitates a thorough chemical and physical study of each composition. This assembled information can be used to maintain safety standards, to prevent costly failures in environmental tests, to re-formulate on a scientific basis for more efficient signal performance, to guide in the development of specifications for the composition, and, in general, to provide a better understanding of the chemical and physical nature of the composition and its behavior under a variety of conditions.

b. Since detailed data on such aspects of the Mk 25 Mod 2 Starter Composition as reaction mechanisms, quantitative chemical analytical methods, and behavior characteristics under a variety of experimental conditions were unavailable, it has been the object of this present investigation to develop as much of this information as was practicable in the laboratory. The results of this investigation, as well as some the instrumentation and methodology employed, are included in this report and a summary of the results appear in a "Data Sheet" in the Appendix, Table I.

c. It is convenient to divide the report into four major sections.

(1) A quantitative analytical scheme for the Mk 25 Mod 2 Starter Composition.

(2) Physical phase changes and chemical reaction mechanisms.

(3) Behavior characteristics under various experimental conditions.

(4) Conclusions.

(a) Section 1

1. In the first section a scheme for the chemical analysis of a typical starter composition of lead dioxide, cupric oxide and crystalline silicon is described. Lead dioxide and cupric oxide are brought into solution by treatment with hot concentrated nitric acid and 30% hydrogen peroxide. The insoluble silicon is removed from the solution by filtration, washed, dried and weighed. From an aliquot of the solution, copper is plated on a platinum cathode and lead dioxide on the anode. From the gain in weight of the respective electrodes, the percentages of cupric oxide and lead dioxide are determined. Volatiles are determined by finding the loss of weight after heating for one hour at 80°C and 5 cm Hg pressure.

2. Such an analytical procedure provides a reliable method of assuring the uniformity of the composition after mixing, as well as determining which, if any, of the components may fall outside the tolerances allowed by the specification.

(b) Section 2

1. The second section is concerned with differential thermal analysis and thermogravimetric analysis of the composition, its individual components and various combinations of these components.

In these techniques samples are heated at a constant rate of temperature rise and the resulting changes, with respect to evolution or absorption of heat in the case of DTA and loss or gain of weight in the case of TGA, are recorded. The data thus obtained indicates something of the nature of the solid state changes, both physical and chemical, which occur in the various components and in the composition as a whole - under experimental conditions. And while experimental conditions are not the same as actual service conditions, data obtained from the experiment will often elucidate aspects of real operation (e.g., stability, ignition point, reaction mechanisms affecting or causing ignition, energy conditions, etc.) Using the data obtained from thermoanalysis, as well as other techniques, an attempt is made to write the chemical reaction equations for the deflagration of this fuel-rich system.

(c) Section 3

1. The third section deals with behavior characteristics of the composition. This includes hazard data, such as impact sensitivity, electrostatic sensitivity and vacuum stability, as well as chemical properties, such as heat of reaction, ignition point and maximum reaction temperature.

(d) Section 4

1. In the final section the results of thermoanalysis studies are discussed with regard to what they reveal concerning the chemical and physical changes occurring before ignition, at ignition and during combustion.

2. ANALYTICAL PROCEDURE FOR MK 25 MOD 2 STARTER COMPOSITION

a. Composition of Mk 25 Mod 2 Starter Formula.

Component	Federal Specification	Parts by Weight	%
Lead Dioxide	JAN-L-376, Grade B	2	20%
Cupric Oxide	MIL-C-13600	3	30%
Silicon	MIL-S-230A, Grade A, Class 2, Average Particle Size 8 - 15 microns	5	50%

b. Determination of Volatile Matter.

(1) Place an accurately weighed sample of about 10 grams in a tared wide mouth weighing bottle. Dry for one hour in a vacuum oven at 5 cm mercury pressure and a temperature of 80°C. Cool in a desiccator, weigh and calculate the percent volatiles:

$$\text{Percent Volatiles} = \frac{\text{Weight Loss X 100}}{\text{Weight of Sample}}$$

c. Solution of Lead Dioxide and Cupric Oxide.

(1) Weigh accurately a sample of about 2.5 grams and transfer to a 250 ml beaker. Treat with 10 ml of distilled water, 50 ml 70% nitric acid, and about 2 ml of 30% hydrogen peroxide added dropwise. Bring the solution to a boil on the hotplate and continue boiling for 5 minutes. Remove the beaker from the hotplate, cool and add another 1 ml portion of 30% hydrogen peroxide dropwise. Heat until the hydrogen peroxide is decomposed, cool slightly and filter through a medium porosity sintered glass crucible that has been tared. Wash with 10 ml hot 70% nitric acid containing five or six drops of 30% hydrogen peroxide. Finally, wash with five 5 ml portions of distilled water. Retain filtrate and washings.

d. Determination of Silicon.

(1) Dry the residue in the tared crucible for two hours at

105°C, or to constant weight, cool in a desiccator and weigh.

$$\text{Percent Silicon} = \frac{\text{Weight of Precipitate} \times 100}{\text{Weight of Sample on a Dry Basis}}$$

e. Electrode position of Copper and Lead Dioxide.

(1) Transfer the filtrate and washings to a 250 ml volumetric flask and dilute to the mark with distilled water. Remove a 100 ml aliquot with a volumetric pipette and transfer to a 250 ml beaker. Add one drop of 1:1 hydrochloric acid. Using a Fisher Electroanalyzer or equivalent with tared platinum electrodes, plate out the copper on the cathode and the lead dioxide on the anode, employing a current of 0.25 amps the first hour, and then 1.5 amps until the copper is completely removed from the electrolyte. Test for copper by removing a small portion of the electrolyte and adding a slight excess of ammonium hydroxide. A blue color indicates incomplete removal of copper.

(2) When all the copper is removed, switch off the power to the stirrer, but leave on the plating current. Remove the electrolyte slowly, washing the electrodes with distilled water as they are exposed to the air. This is to remove the acid before it can attack the copper. If any black lead dioxide has been shaken off the anode, it must be captured by filtering the electrolyte through a tared sintered glass crucible, washing, drying, and weighing. Rinse the electrodes with ethyl alcohol, then acetone, and finally dry in air for three minutes. Weigh cathode for copper, anode for lead dioxide.

$$\text{Percent CuO} = \frac{\text{Increase in Weight of Cathode} \times 1.2518 \times 100 \times 2.5}{\text{Weight of Sample on Dry Basis}}$$

$$\text{Percent PbO}_2 = \frac{\text{Increase in Weight of Anode} \times 2.5 \times 100}{\text{Weight of Sample on Dry Basis}}$$

(3) Since there is a possibility of losing PbO_2 from the anode, check the value for PbO_2 found by electrode position against the value obtained by subtracting the sum of the values for silicon, copper oxide and volatiles from 100%.

3. PHYSICAL PHASE CHANGES AND REACTION MECHANISMS

a. DTA and TGA were employed to study the various physical and chemical changes occurring in the Mk 25 Starter Composition under the experimental conditions prevailing in each of these techniques. Both techniques involve heating the sample at a more or less constant rate. In DTA any change in the sample, involving the evolution or absorption of heat as the temperature of the sample is progressively raised, are recorded as exothermic or endothermic peaks. TGA shows any weight changes which the sample undergoes as the temperature of the sample is progressively elevated to the appropriate limit. Thus, in DTA, any chemical or physical change in the sample which results in either a loss or a gain of total heat in the sample can be recorded; moreover, the temperature at which these changes occur, and the magnitude of the changes, can be approximated. However, the many variables encountered in DTA make it difficult to compare results of different types of instruments in different laboratories. TGA results are less subject to this disadvantage.

b. DTA and TGA studies were performed on the Mk 25 Starter Composition and its components to discover what changes in energy state and weight occurred as the samples were heated to their ignition point. It should be remembered, in comparing DTA and TGA results on the same sample, that they will not always correlate in every particular due to the different experimental conditions. In DTA the sample is packed in a sample well and the air available to it is limited. In TGA the sample is loosely packed and fully exposed to the air. These conditions often affect the results obtained by the different techniques.

c. Differential thermal analysis and thermogravimetric analysis thermograms for the Mk 25 Mod 2 Starter Composition and its components appear in the Appendix (q. v.). Thermoanalysis reveals that the Pb-Si couple is reactive at a lower temperature than the CuO-Si couple. Figure A shows that PbO_2 decomposes in two stages. The first stage, which occurs between 350°C and 450°C, is represented by the reaction:

$$2PbO_2 = Pb_2O_3 + O.$$

The second stage, occurring between 450°C and 550°C, is represented by the equation:

$$Pb_2O_3 = 2PbO + O.$$

d. Endothermic peaks obtained by DTA (Figure 4) confirm the TGA weight losses shown in Figure A: a large peak occurs at about 450°C and another at about 550°C. Thermograms indicate that the silicon (Figures 5 and C) and the cupric oxide (Figures 6 and B) components are stable at temperatures up to and exceeding the ignition point of the system.

e. The ignition point of the PbO_2-Si couple appears in Figure 2 (DTA thermogram) and Figure D (TGA thermogram) at about 470°C. The CuO-Si couple is shown in Figure 3 and Figure E. This couple reacts at a much higher temperature - 700°C in the DTA thermogram. The weight gain shown in the TGA thermogram (Figure E) is due to the combination of reduced copper with oxygen in the air. DTA and TGA results are, in this instance, in good agreement.

f. From the data, then, it is clear that ignition is due to the reaction of the PbO_2-Si couple. The heat generated by this reaction immediately initiates the ignition of the CuO-Si couple, and the two reactions then proceed simultaneously but not at the same rate. The ignition point of the composition as a whole is somewhat higher than the ignition of the PbO_2-Si couple. TGA results (Figure F) show the ignition point to be about 480°C, whereas the DTA results (Figure 1) reveal a peak at 540°C, although exothermic action undergoes a pause at about 470°C followed by a rapid acceleration. This higher ignition point is probably due to a dilution effect that the copper oxide has on the crucial PbO_2-Si couple.

g. The two reactions that occur upon ignition and then proceed during combustion are the following:

$$PbO_2 + Si = Pb + SiO_2 + 151{,}800 \text{ cal/mole}$$

$$2CuO + Si = 2Cu + SiO_2 + 136{,}780 \text{ cal/mole.}$$

That these are the correct reactions is confirmed by the fact that the theoretical thermodynamic value for the free energy of the reaction (384.3 cal/g) compares closely with the experimentally determined heat of reaction (375.5 cal/g).

4. BEHAVIOR CHARACTERISTICS UNDER VARIOUS EXPERIMENTAL CONDITIONS

a. In order to prepare a data sheet, values were obtained in the laboratory for such standard behavior characteristics as impact sensitivity, electrostatic sensitivity, vacuum stability, heat of reaction, ignition point, etc. Instrumentation, procedures and interpretation of results obtained in these standard tests appear in NADC RDTR No. 16, Section III.

(1) Impact sensitivity* is determined by finding the average height at which a 10 mg sample, pressed in a copper cup at 5000 psi, detonates when struck by a falling 2 kg weight. In this instance, no fires were observed from 20 cm to 50 cm in increments of 2 cm.

(2) Electrostatic sensitivity* is determined by using the Pittman-Dunn Tester. The apparatus, as well as additions and modifications made to it, is discussed in NADC RDTR No. 18. In the present series of tests, 0.02 microfarad capacitance was used. Testing 30 mg samples, no fires resulted at 220, 240, 260, 300, 500, 1000, 1500, 2000, 2500, 3000, 3500, and 4300 volts. The material was not scattered by the spark when tested.

(3) Ignition point. Under different conditions, the ignition point of the composition varied to some extent.

(a) By DTA, heating rate 20°C/min in limited air = 540°C ± 15°C.

(b) By TGA, heating rate 16°C/min average in air = 480°C ± 10°C.

(c) By 5 sec immersion of 15 mg sample in molten metal bath = 560°C ± 20°C.

(4) Heat of Reaction.

(a) Theoretical value = 387 cal/g assuming the following reactions:

$$PbO_2 + Si = Pb + SiO_2 + 151,800 \text{ cal/mole}$$

$$2CuO + Si = 2Cu + SiO_2 + 136,780 \text{ cal/mole.}$$

(b) Experimental value, determined in the calorimeter under argon gas = 375.6 cal/g.

(5) Maximum reaction temperature exceeds the range of the Hoskins Pyrometer (1400°C). Since a piece of 32 gauge platinum wire was fused by the heat of reaction, the reaction temperature is greater than the melting point of platinum (1769°C), and is estimated to be in the range of 3000°C.

(6) Gas evolved. The reaction was carried out in a Parr calorimeter bomb which was sealed. After cooling to room temperature, the bomb was opened and the gas bled into a gas measuring apparatus. The volume of gas evolved upon reaction of the composition, and not condensed after cooling at room temperature = negligible. However, gases may be evolved in the high temperature reaction which condense upon cooling.

(7) Vacuum stability*. Using 2.5 g samples, a bath temperature of 110.3 - 110.9°C, and a time of 18.5 hours, the average volume of gas formed was 0.18 ml corrected to STP. This indicates negligible decomposition.

5. CONCLUSION

a. It has been the object of this investigation to explore the chemical and physical characteristics of the Mk 25 Mod 2 Starter Composition and to collect all pertinent information into a data sheet.

b. Agreement between the theoretical thermodynamic value for

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* Tests performed by R. Ilger

the heat of reaction, ΔH, and the experimentally determined calorific value, indicates that the reaction mechanism which occurs during the deflagration of the starter composition may be represented by the two equations:

$$PbO_2 + Si = Pb + SiO_2 + 151{,}800 \text{ cal/mole}$$

$$2CuO + Si = 2Cu + SiO_2 + 136{,}780 \text{ cal/mole.}$$

c. Thermochemical methods, including differential thermal analysis and thermogravimetric analysis, indicate that ignition is dependent upon the reaction between the PbO_2-Si couple and that the CuO-Si couple moderates the reaction and reacts itself only after a high temperature is reached. Ignition occurs due to the thermal decomposition of lead dioxide in the temperature range of 400 - 450°C according to the following equation:

$$2PbO_2 = Pb_2O_3 + O.$$

However, the dilution and moderation effect of the CuO elevates the actual ignition and propagative deflagration to a temperature range of approximately 500°C. This can be seen by comparing the thermogram of the Mk 25 Mod 2 Starter Composition formula (2L-3C-5S) shown in Figure 1 with the thermogram of the lead dioxide-silicon couple (2L-5S) shown in Figure 2. The ignition point of the first is 540°C, but with the lead dioxide - silicon couple it is only 460°C.

d. Data on the behavior characteristics of the Mk 25 Mod 2 Starter Composition is summarized in the Data Sheet in the Appendix.

APPENDIX

TABLE I

DATA SHEET - MK 25 MOD 2 STARTER COMPOSITION

1. Formula

Lead Peroxide	PbO_2	20 ± 0.5%	JAN-L-376, Grade B
Cupric Oxide	CuO	30 ± 0.5%	MIL-C-13600
Silicon	Si	50 ± 0.5%	MIL-S-230, Grade A, Class 2

2. Specification: BUWEPS Dwg. No. 2150073, Rev. B, of LD No. 282857

3. Performance: Not documented.

4. Loading Pressure: None; packed loose.

5. Calorific Value:

   a. 380 cal/g = Experimental Calorimetric Value
   b. 387 cal/g = Theoretical Thermodynamic Value

6. Ignition Point:

   a. By DTA, heating rate 20°C/min, limited air = 540°C ± 15°C
   b. By TGA, heating rate 16°C/min, ample air = 480° ± 10°C
   c. By 5 sec immersion of 15 mg sample in molten bath = 560°C ± 20°C

7. Maximum Reaction Temperature: Exceeds the melting point of platinum at 1769°C; estimated value = 3000°C.

8. Gas Evolution: Negligible.

9. Electrostatic Sensitivity: No fires up to 4300 volts at 0.02 uf.

10. Impact Sensitivity: No fires observed between 20 and 50 cm in 2 cm increments.

11. Vacuum Stability: For 2.5 g sample = 0.18 ml corrected to STP.

12. Thermogravimetric Analysis: See Section II of this report and thermograms in the Appendix.

13. Differential Thermal Analysis: See Section II of this report and thermograms in the Appendix.

14. Principal Reaction Equations:

   a. $PbO_2 + Si = Pb + SiO_2$ + 151,800 cal/mole
   b. $2CuO + Si + 2Cu + SiO_2$ + 136,780 cal/mole.

15. Quantitative Chemical Analysis: See RDTR No. 27, "Chemical Analysis of a Typical 6-6-8 Pyrotechnic Starter Composition", 13 July 1962.

16. Health Hazards: Probable formation of lead vapor during combustion; for comprehensive discussion of toxicology and dangers see N. I. Sax, *Dangerous Properties of Industrial Materials*, under any of the applicable headings: lead; lead dioxide; copper; copper oxide; silicon.

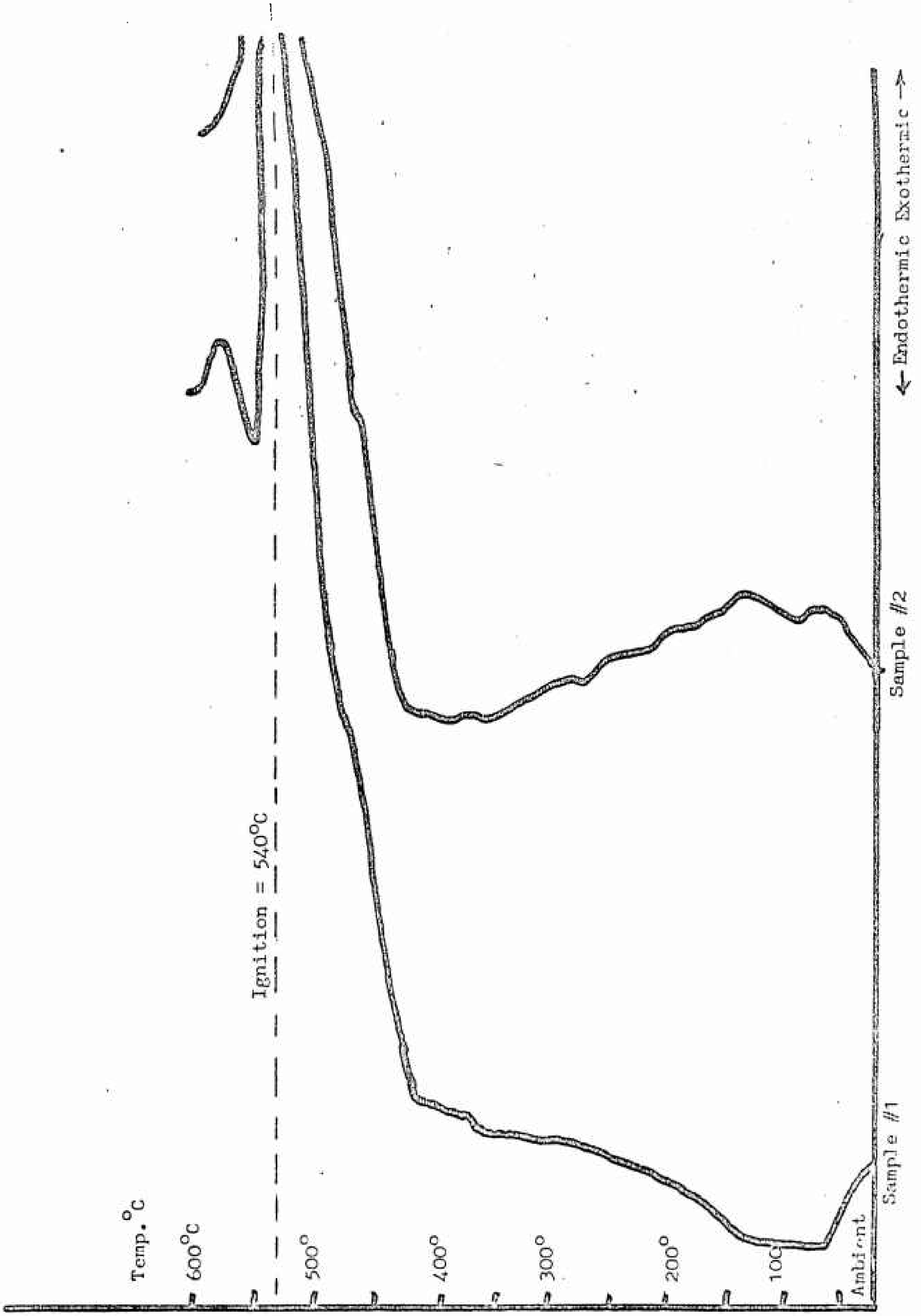

FIGURE 1: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPOSITION

Heating rate = 20°C/min
Sensitivity = 25%

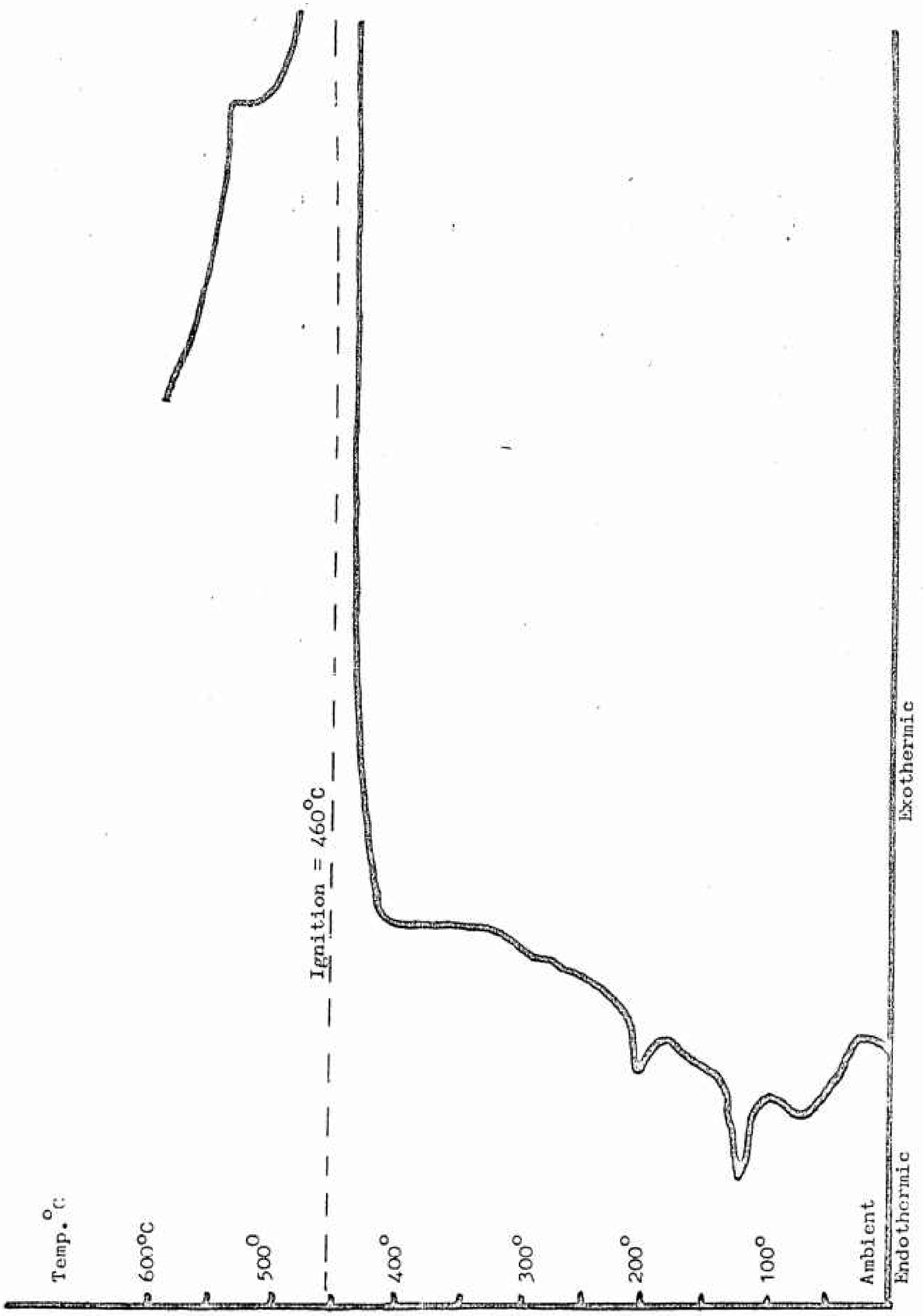

FIGURE 2: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENTS: 2 PARTS LEAD DIOXIDE TO 5 PARTS SILICON BY WEIGHT

20°C/ min
25% Sensitivity

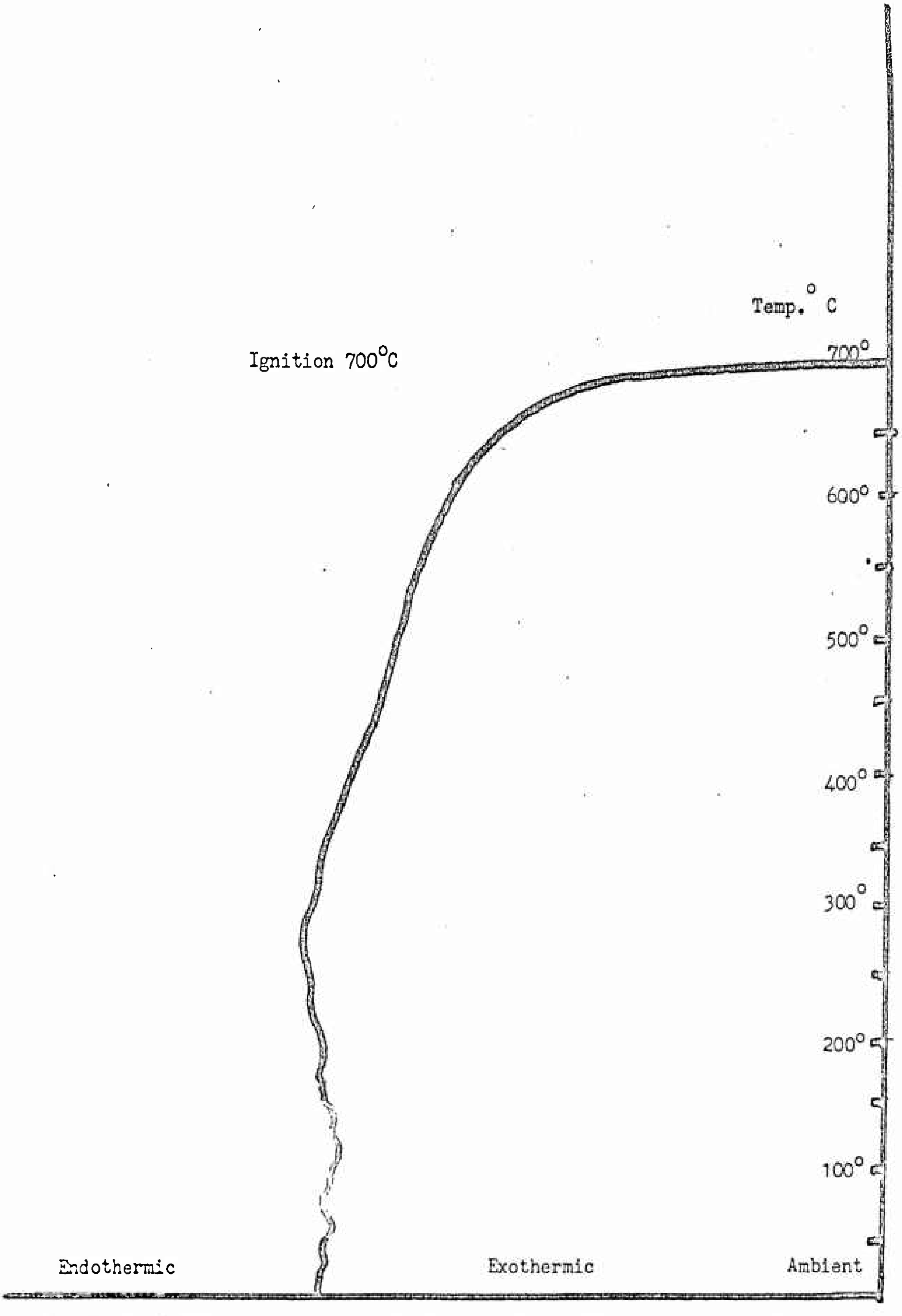

FIGURE 3: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENTS: 3 PARTS CUPRIC OXIDE TO 5 PARTS SILICON BY WEIGHT

20°C/ min
25% Sensitivity

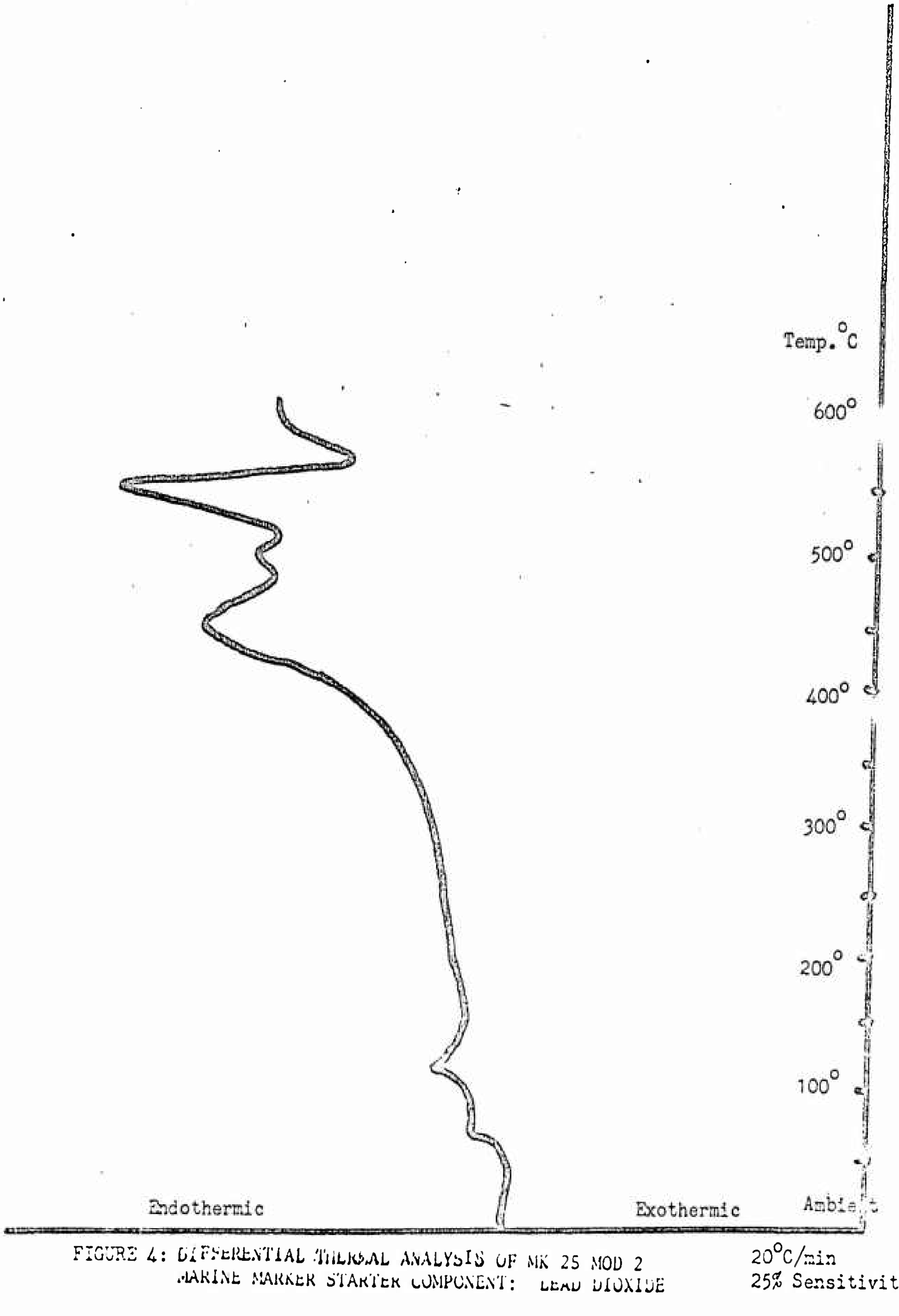

FIGURE 4: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2
MARINE MARKER STARTER COMPONENT: LEAD DIOXIDE

20°C/min
25% Sensitivity

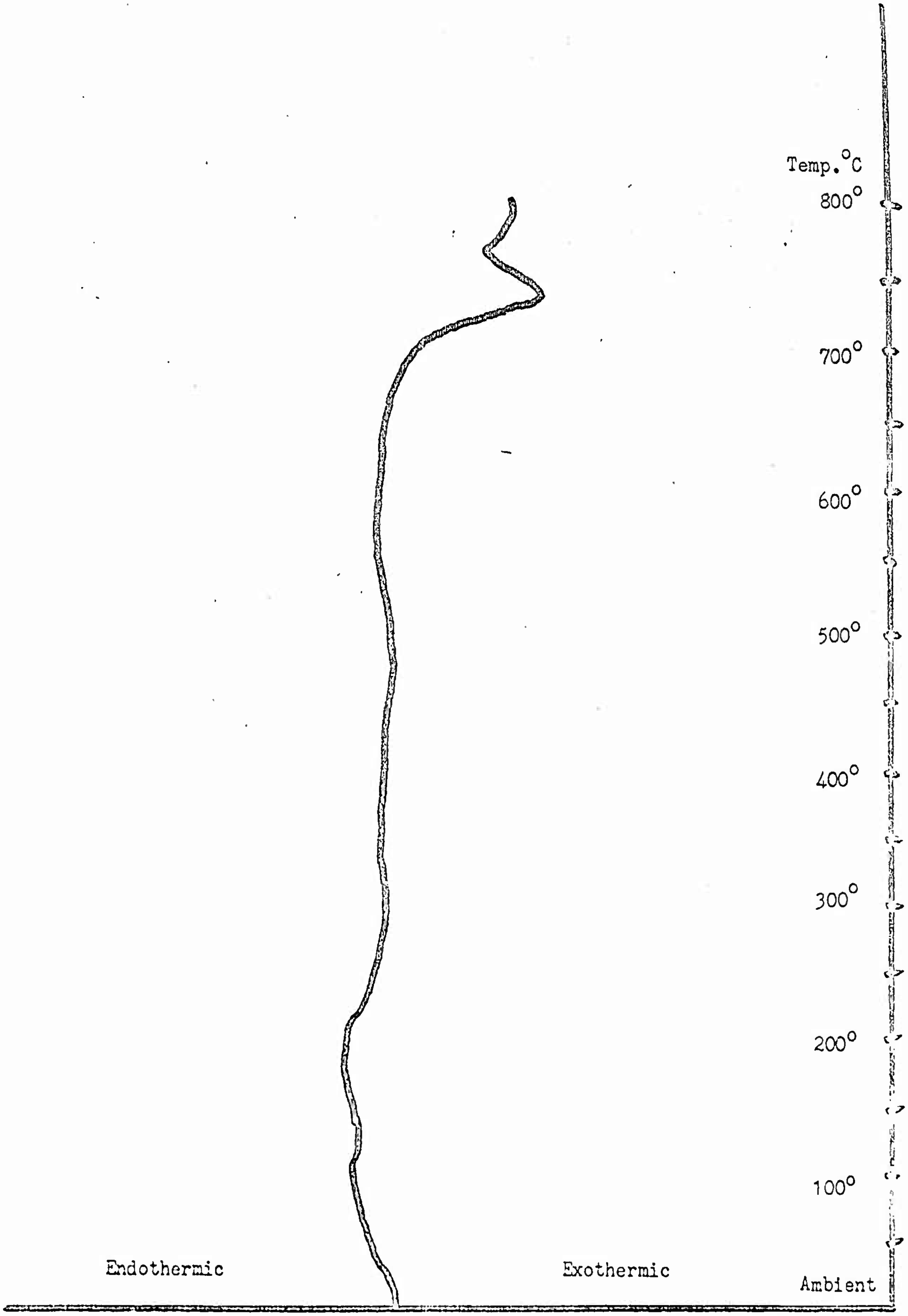

FIGURE 5: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENT: CUPRIC OXIDE

20°C/min
25% Sensitivity

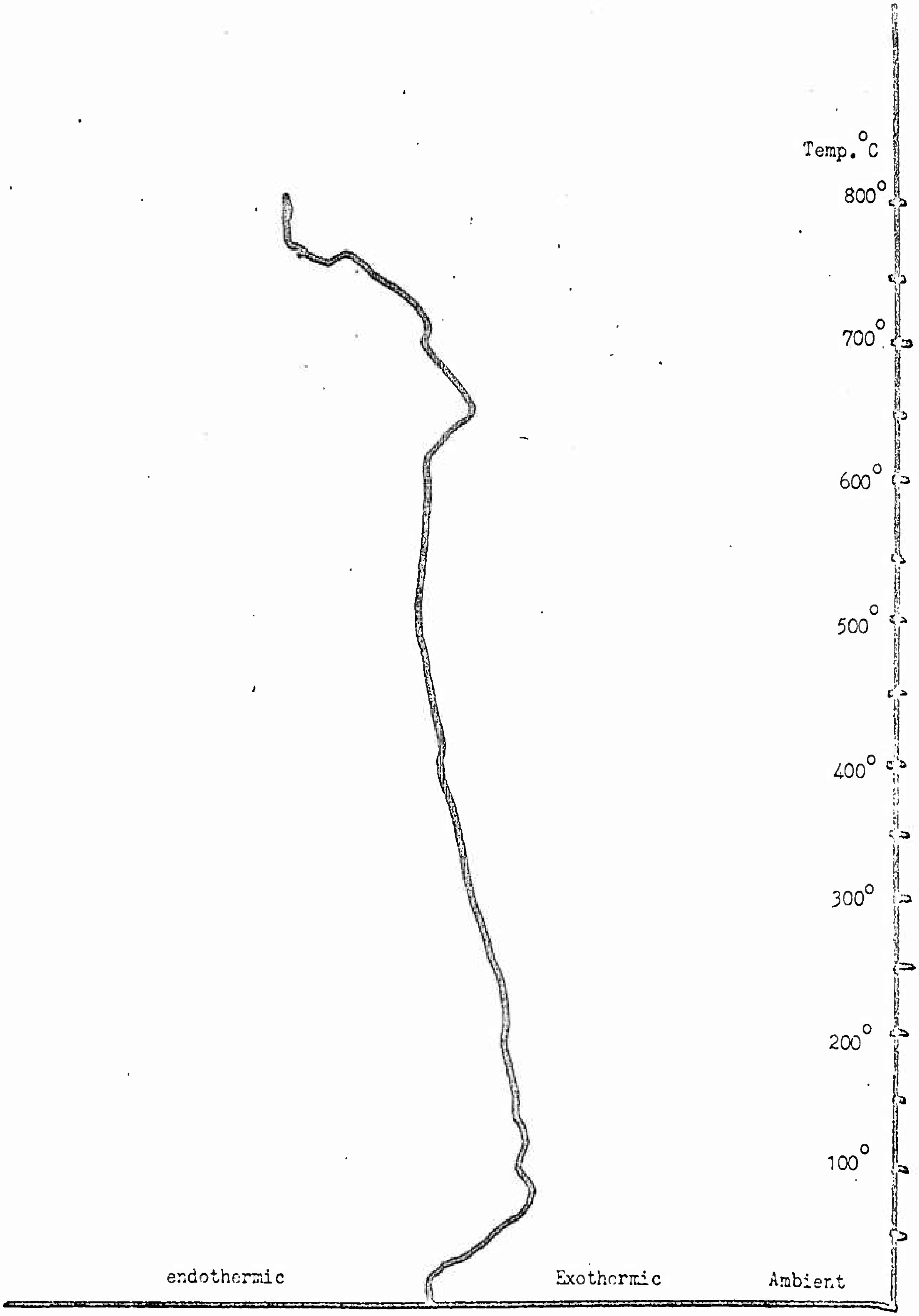

FIGURE 6: DIFFERENTIAL THERMAL ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENT: SILICON

20°C/min
25% Sensitivity

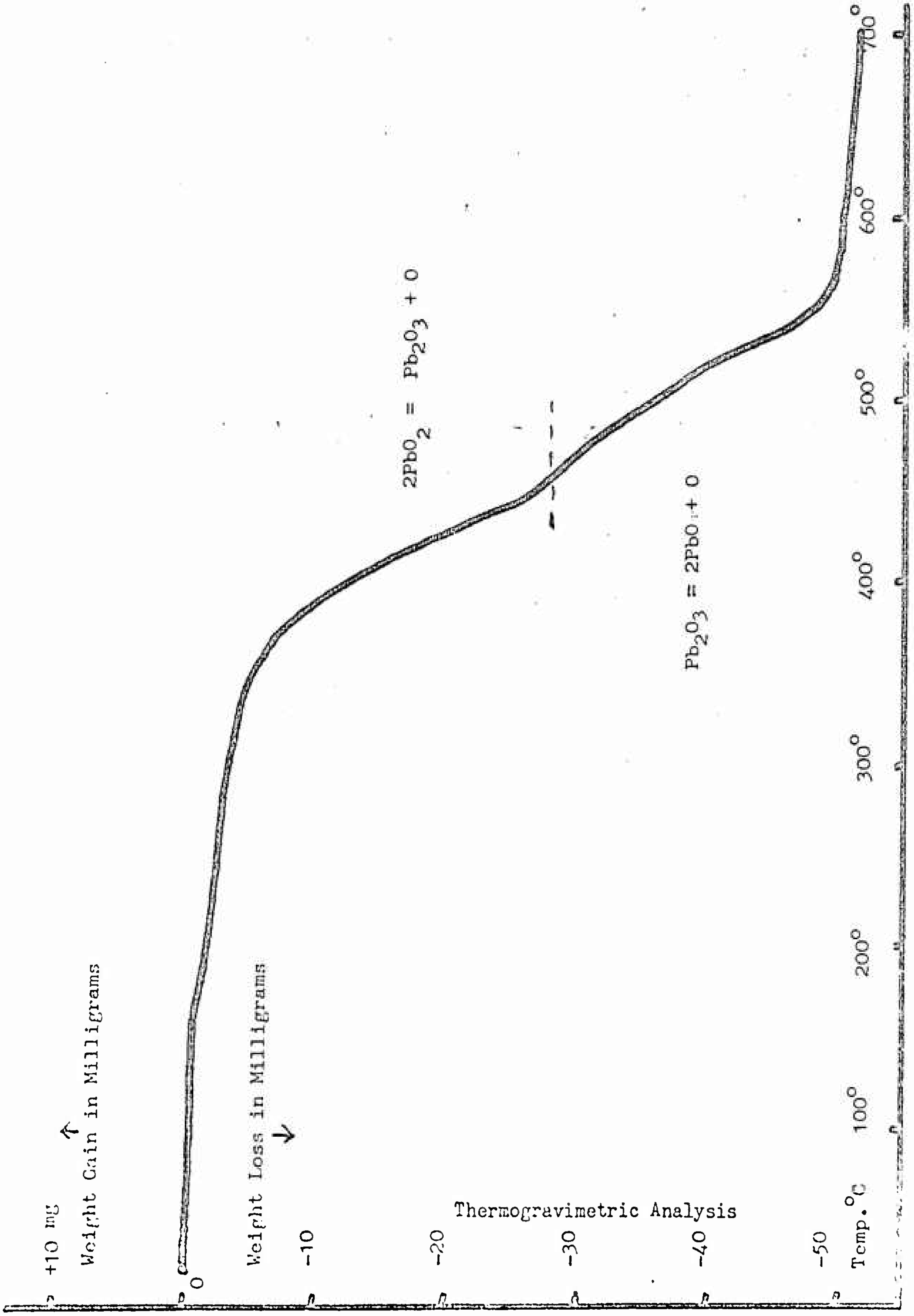

FIGURE A: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2 MARINE MARKER COMPONENT: LEAD DIOXIDE

Heating Rate= 16°C/min
Sample Weight= 749 mg

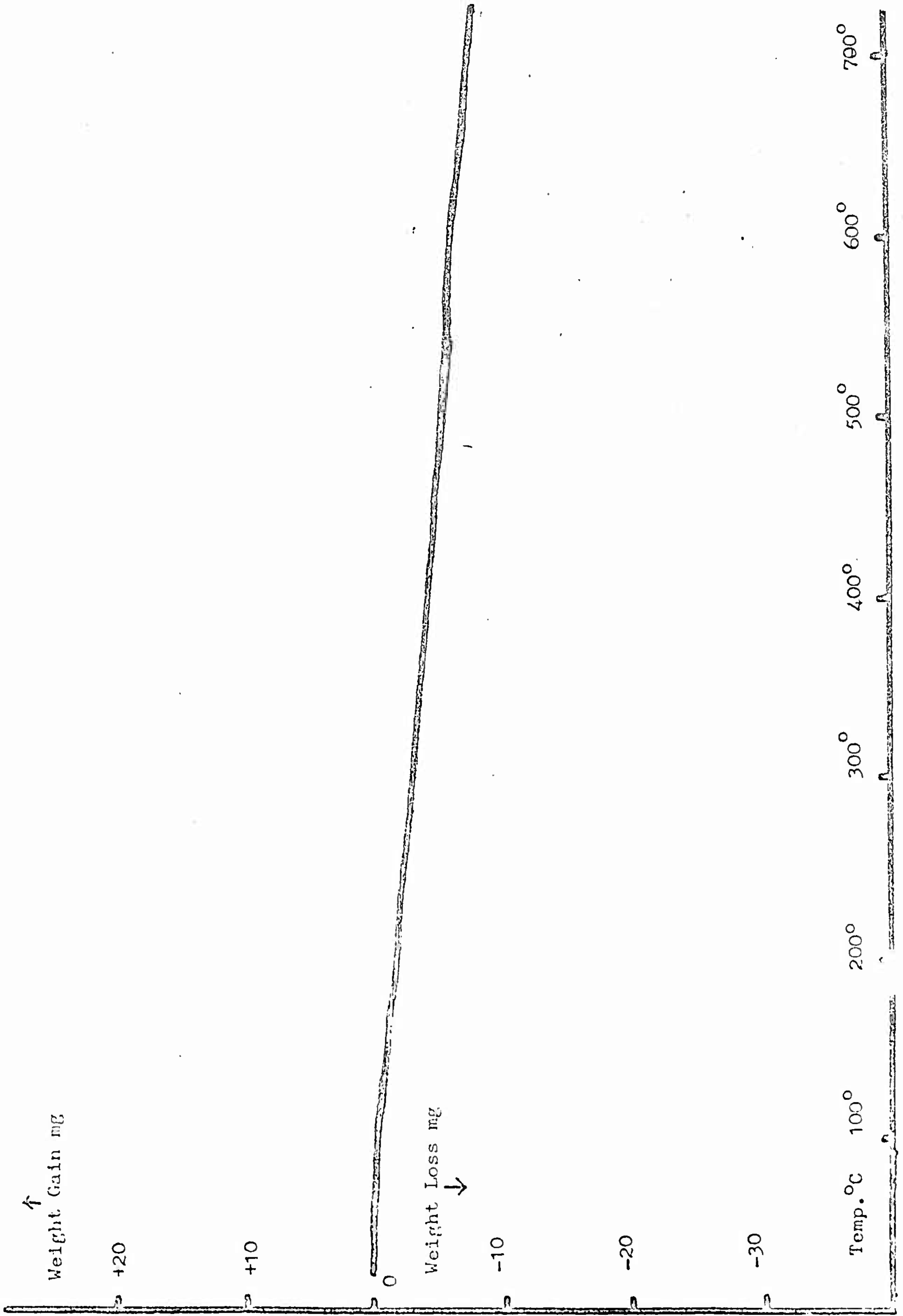

FIGURE B: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2 16°C/min
MARINE MARKER COMPONENT: CUPRIC OXIDE 760 mg

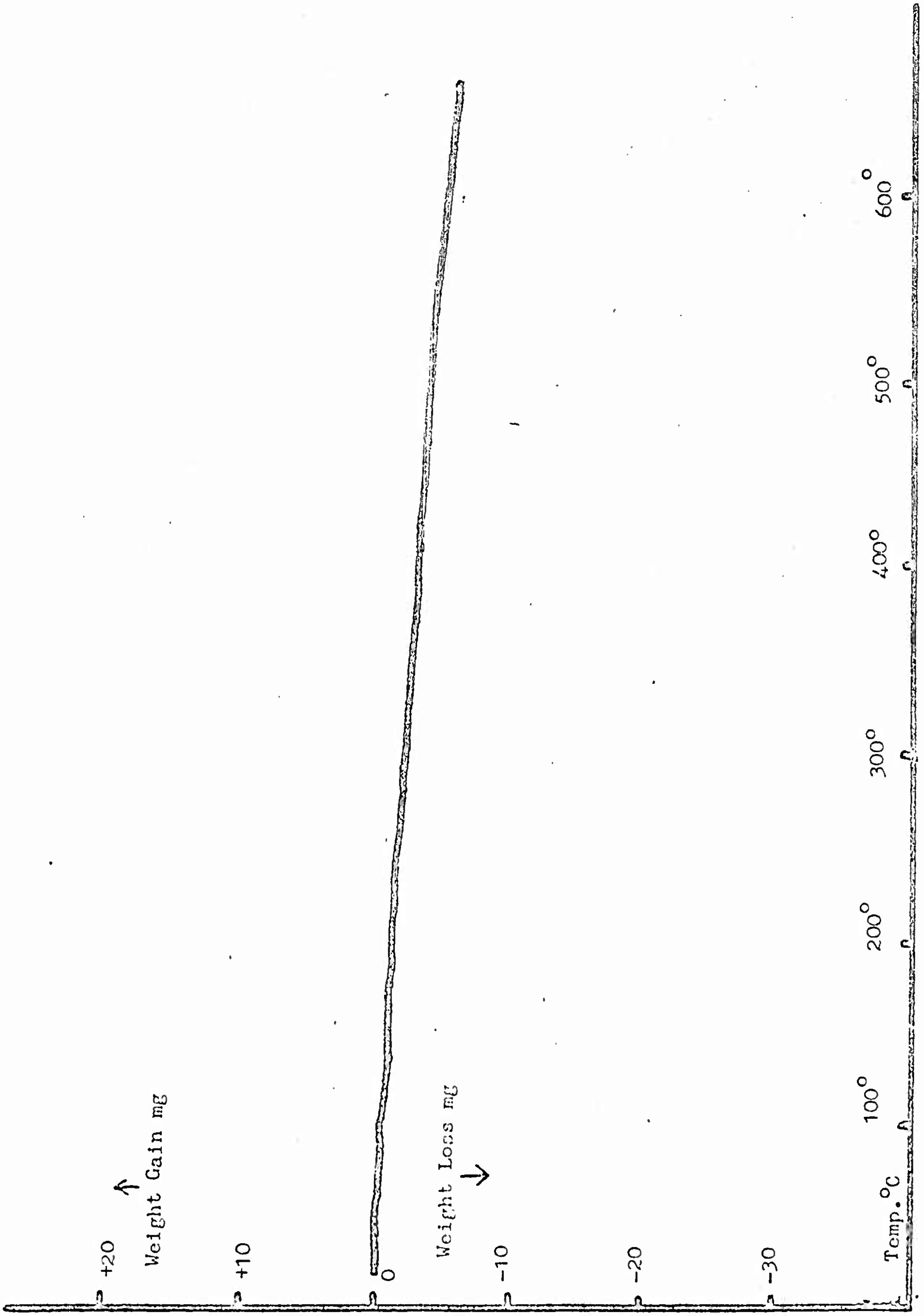

FIGURE C: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2 MARINE MARKER COMPONENT: SILICON

16°C/min
634 mg

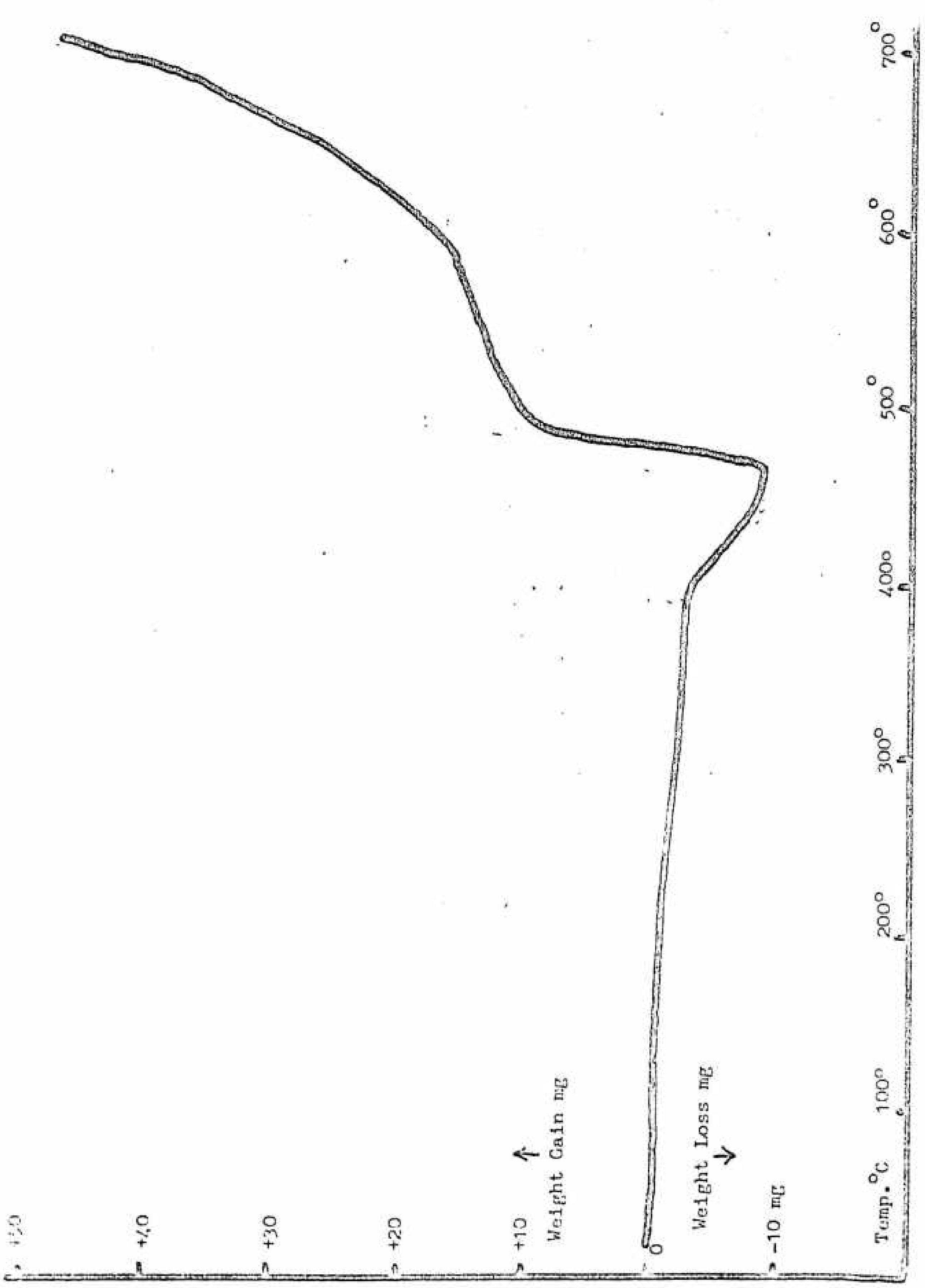

FIGURE D: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENTS: 2 PARTS LEAD DIOXIDE TO 5 PARTS SILICON BY WEIGHT

16°C/min
780 mg

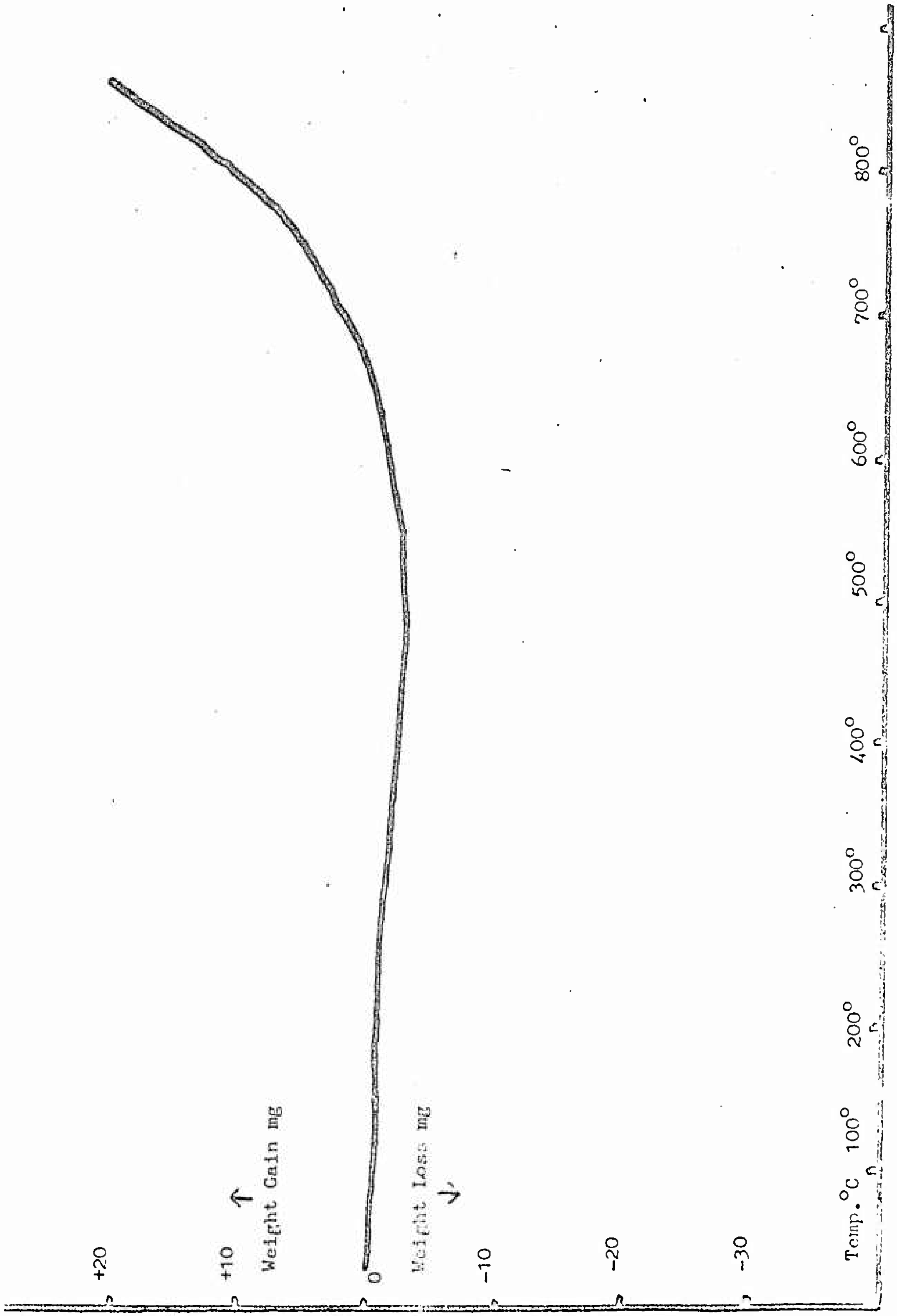

FIGURE E: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2 MARINE MARKER STARTER COMPONENTS: 3 PARTS CUPRIC OXIDE TO 5 PARTS SILICON BY WEIGHT

16°C/min
799 mg

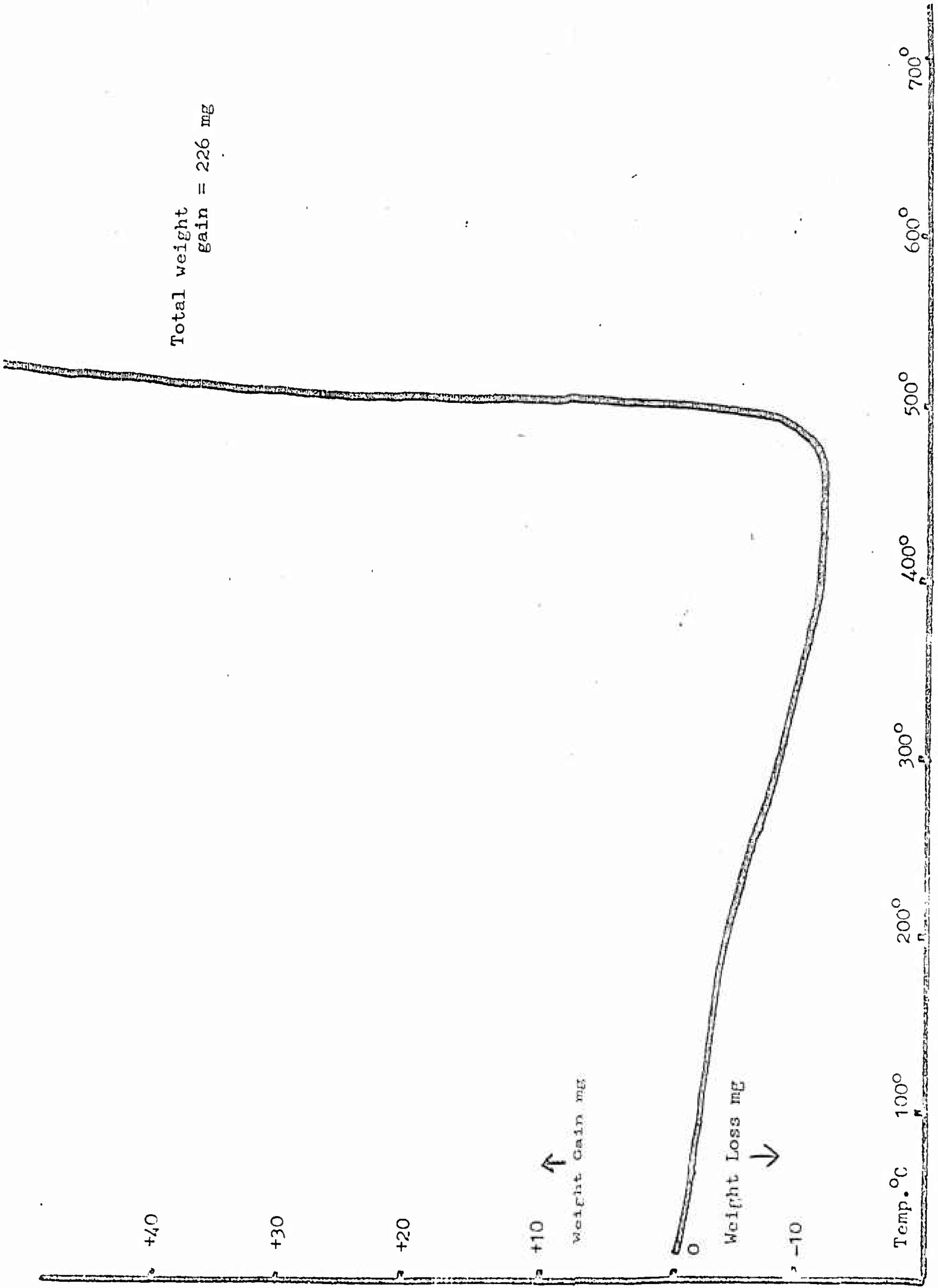

FIGURE F: THERMOGRAVIMETRIC ANALYSIS OF MK 25 MOD 2
MARINE MARKER STARTER COMPOSITION

16°C/min
775 mg

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