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THERMOGRAVIMETRIC ANALYSIS OF SILVER OXIDE MIXTURES

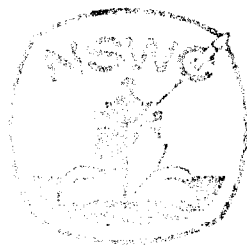
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RESEARCH AND TECHNOLOGY DEPARTMENT

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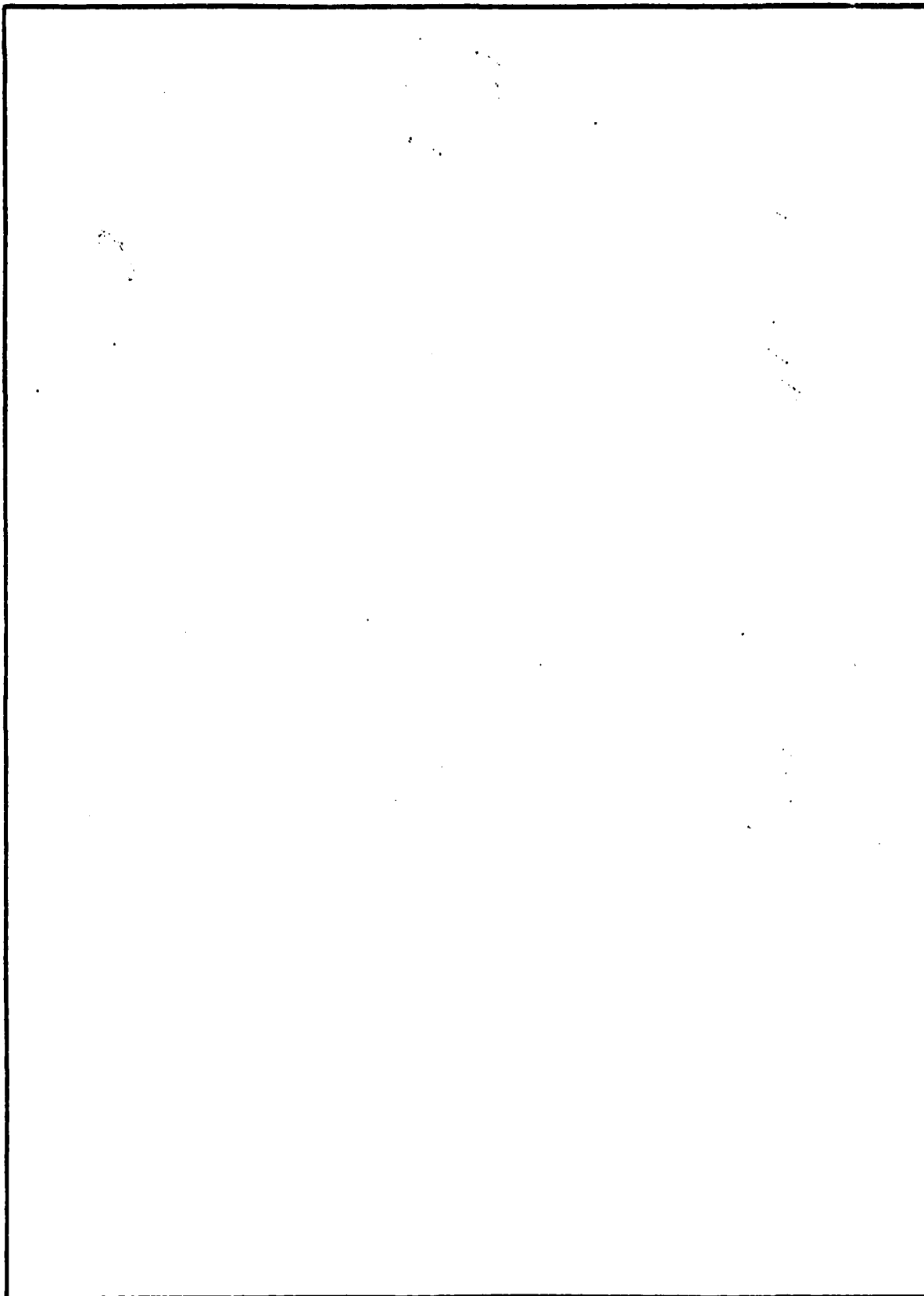
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INTRODUCTION

Alkaline silver oxide-zinc batteries, both primary and secondary, have found widespread use in military applications. The silver oxide cathode has also found use in other battery systems. A well documented problem in the use of silver oxide cathodes is the degradation of the silver (II) oxide active cathode material. To a lesser extent, the silver (I) oxide present in electroformed cathodes also degrades. The rate of degradation of both oxides depends on the method of preparation and is a function of several parameters including time and temperature.

In this paper we report the development of a new thermogravimetric analysis (TGA) technique for determining the AgO , Ag_2O , and Ag content of silver oxide cathode material. Also, the technique is compared with the currently accepted method of silver oxide cathode analysis, the Wagner titration method.

TGA METHOD

Several methods of analysis have been proposed and are in current use for the determination of silver-silver oxide mixtures: 1) chemical titration, 2) isothermal decomposition, 3) gasometric methods, 4) electrochemical or chemical methods, and 5) X-ray diffraction. The chemical titration methods proposed by F. Jirsa¹ and R. D. Wagner² involve several analysis steps for determination of the three components. The crucible method,³ an isothermal decomposition method, and a modification of this method proposed by J. J. Lander⁴ involve two

¹Klausmeier, R. E., Ed., An Analytical Method for the Determination of Argentic Oxide (AgO) and Silver Oxide (Ag_2O) in Zinc-Silver Oxide Batteries, Report No. QE/C 61-44, QEL/NAD, Crane, Indiana, Mar 1961, p. 2.

²Wagner, R. D., A Method for the Quantitative Analysis of the Silver Oxide Cathode, NOL TR 64-214, Aug 1965.

³Klausmeier, Determination of Argentic Oxide (AgO) and Silver Oxide (Ag_2O).

⁴Lander, J. J., Bourne, W. C., and Logsdon, J. W., Report on Positive Plate Analyses of Cells from Minuteman Zinc-Silver Oxide Reserve Batteries, AFAPL-POE-76-19, Aug 1976.

isothermal decompositions in an air atmosphere. In the gasometric method, proposed by F. M. Bowers, et al.,⁵ the oxygen evolved upon isothermal decomposition of the oxides is measured at four different temperatures. Other electrochemical methods such as coulometric titration have been suggested. The basic problem with the possible electrochemical or chemical methods is that the sample composition changes during the course of analysis. All of these methods require several hours for sample preparation and complete analysis, and many involve tedious measurements and complex apparatus. X-ray diffraction analysis, though less time consuming, is accurate to only +10%. Furthermore, it is believed that X-rays may decompose the silver oxides.

In an attempt to discover a more rapid, precise method of analyzing silver-silver oxide mixtures, we explored thermogravimetric analysis (TGA). TGA is a technique in which the change in sample mass is measured as a function of temperature. It is a well-established analytical method⁶ for substances or mixtures which either decompose into or react with a gas, with a resultant change in mass. In the study of silver oxide cathode material, oxygen is liberated upon thermal decomposition of both silver (I) and silver (II) oxides.



Our measurements showed that the temperatures of maximum decomposition rates were near 460K (187°C) for AgO and near 630K (357°C) for Ag₂O. This large temperature separation was the basis for the quantitative analysis of three-component AgO, Ag₂O, Ag mixtures by TGA.

Previous TGA techniques for AgO, Ag₂O, Ag mixtures^{7,8} were based on the isothermal decomposition of samples in an air atmosphere. Samples were held at two preselected temperatures until the decomposition of each oxide was judged to be complete. The major problem with these techniques was the complication introduced by the small but measureable and well-known simultaneous decomposition of the two oxides at temperatures between those of their maximum decomposition rates. The long analysis time (2-4 hrs.) required for these methods rendered them unsuitable for our purposes.

⁵Bowers, F. M., Wagner, R. D., Berlat, N. R. and Cohen, G. L., The Decomposition of Argentic and Argentous Oxides in Concentrated KOH Electrolyte, NOL TR 62-187, Apr 1963.

⁶Wendlandt, W. W., Thermal Methods of Analysis, (New York: John Wiley & Sons, Inc., 1974), pp. 99-133.

⁷Klausmeier, Determination of Argentic Oxide (AgO) and Silver Oxide (Ag₂O).

⁸Lander, et al., Positive Plate Analyses of Cells from Minuteman.

To address these problems, we developed a technique employing a DuPont 1090 Thermal Analysis System with a 951 Thermogravimetric Analyzer (TGA). The major advantage of this technique is that the mass change as a function of temperature is continuously monitored throughout both decompositions, yielding a TGA "signature" for the sample. In an attempt to solve the simultaneous decomposition problem discussed earlier, it was found advantageous to monitor the first derivative of the mass change with time, in addition to the primary TGA curve. Since the derivative curve is a measure of the decomposition rate, we theorized that the minimum in the curve should correspond to the point of minimum decomposition rate of both oxides. This point was therefore chosen as the best approximation for the completion of AgO decomposition and the initiation of Ag₂O decomposition (See Figures 4 and 5). We used this data point together with the initial and final sample weights for calculating the composition of AgO, Ag₂O, Ag mixtures. A derivation of the equations used to calculate the composition is presented in Appendix A.

DSC METHOD

Differential scanning calorimetry (DSC) was studied as a complementary method to TGA. DSC is a technique in which the heat flow into or out of a sample is measured as a function of temperature. In DSC, all changes in the enthalpy of the sample, not just those associated with a mass change, are measured. Furthermore, transition temperatures can be determined more accurately with DSC.

EXPERIMENTAL

A DuPont 1090 Thermal Analysis System with a 951 Thermogravimetric Analyzer (TGA) and a Differential Scanning Calorimeter (DSC) was used for this study. TGA and DSC were run over a temperature range of 303K to 823K (30° to 550°C) at a heating rate of 20K/min in a flowing atmosphere (40 ml/min) of dry argon. TGA samples were run in platinum boats. DSC samples were weighed on a Cahn Electrobalance (Model G) and run in uncovered aluminum pans. The TGA was calibrated with calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and the DSC was calibrated with standard pure indium metal. Typically, a TGA run using the new method, including sample preparation and data analysis, was completed in less than one hour.

The samples were silver metal, "pure" silver oxides, mixtures of these, and samples of silver oxide cathode material obtained from various battery manufacturers. Silver (I) oxide was supplied by Fisher Scientific Co. (purified), Alfa Products (99%), and Metz Metallurgical Corp. (99.6%). Silver (II) oxide was obtained from Alfa Products (94%) and Metz Metallurgical Corp. (95%). Powdered silver metal was supplied by Fisher Scientific Co.

Samples of cathode material were prepared by removing all of the active material from the current collector, mixing it, and then using portions of this homogeneous material. Sample sizes for TGA and DSC were typically 70-80 mg and 10 mg, respectively. The precision of weighing was $\pm 0.01\%$ for TGA and $\pm 0.1\%$ for DSC.

Four samples of cathode material were analyzed by both TGA and the Wagner chemical titration method.⁹ The Wagner method was performed at NSWC, Crane, Indiana. In addition, NSWC performed a standard acidification/gasometric analysis technique for the determination of Ag_2CO_3 as CO_2 .

RESULTS AND DISCUSSION

TGA curves of AgO , Ag_2O , and Ag are presented in Figure 1. (The Ag_2O and AgO samples described below were all obtained from Metz Metallurgical Corp.) The curve of Ag is featureless, as expected, showing the absence of any oxidation of the silver sample. The slight apparent mass increase (0.06%) is caused by a buoyancy effect as the argon purge gas is heated and its density decreases. The total mass loss on the AgO curve (13.10%) is in good agreement with the calculated value of 12.92% for pure AgO . The mass losses for the two decomposition steps of pure AgO are theoretically identical (equations 1 and 2). Thus, the completion of the first decomposition process is theoretically located on the curve near 93.50% (or 6.5% oxygen loss at approximately 360°C). On the Ag_2O curve, the total mass loss (7.10%), again, agrees well with the calculated value of 6.90% for pure Ag_2O . A small mass loss (0.10%) beginning at about 160°C is visible on the curve from the decomposition of the AgO impurity in the Ag_2O sample. This small mass loss is more evident in the derivative curve.

A typical TGA curve of a mixture of AgO and Ag_2O is shown in Figure 2. By choosing the point at which the decomposition of AgO to Ag_2O was complete (Figure 1B), 360°C , the composition of the mixture was determined. The Ag_2O decomposition portion of the curve has an inflection that is more clearly seen as a dual peak in the derivative curve. This phenomenon has been attributed to the difference in particle size of the two "types" of Ag_2O in the sample, the Ag_2O formed from the decomposition of AgO (peak 1) and that initially present (peak 2). Their decomposition temperatures can differ by as much as 20°C . The same temperature shift in the derivative peaks is seen by comparing Figures 1B and 1C. The final horizontal plateau is reached upon total decomposition of the sample to metallic silver.

It was found that silver catalyzed the decomposition of Ag_2O . Decomposition began at progressively lower temperatures (Figure 3) as the silver metal content was increased. Because the silver powder was more dense and larger in particle size than the two oxides, uniform ternary mixtures were difficult to prepare and sample. For this reason, silver was excluded from mixtures of the two oxides during this part of the study to verify the procedure.

⁹Wagner, Quantitative Analysis of the Silver Oxide Cathode.

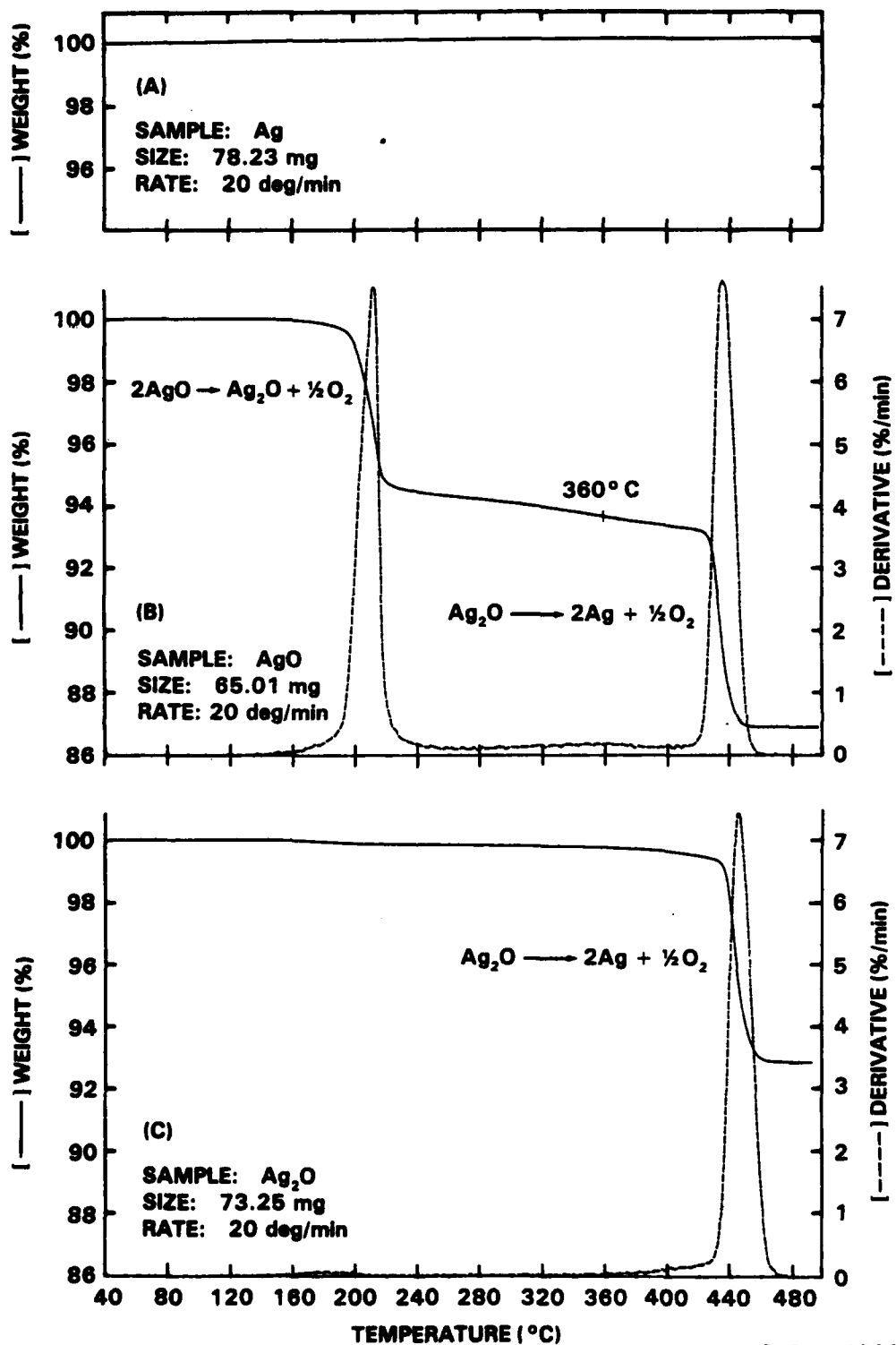
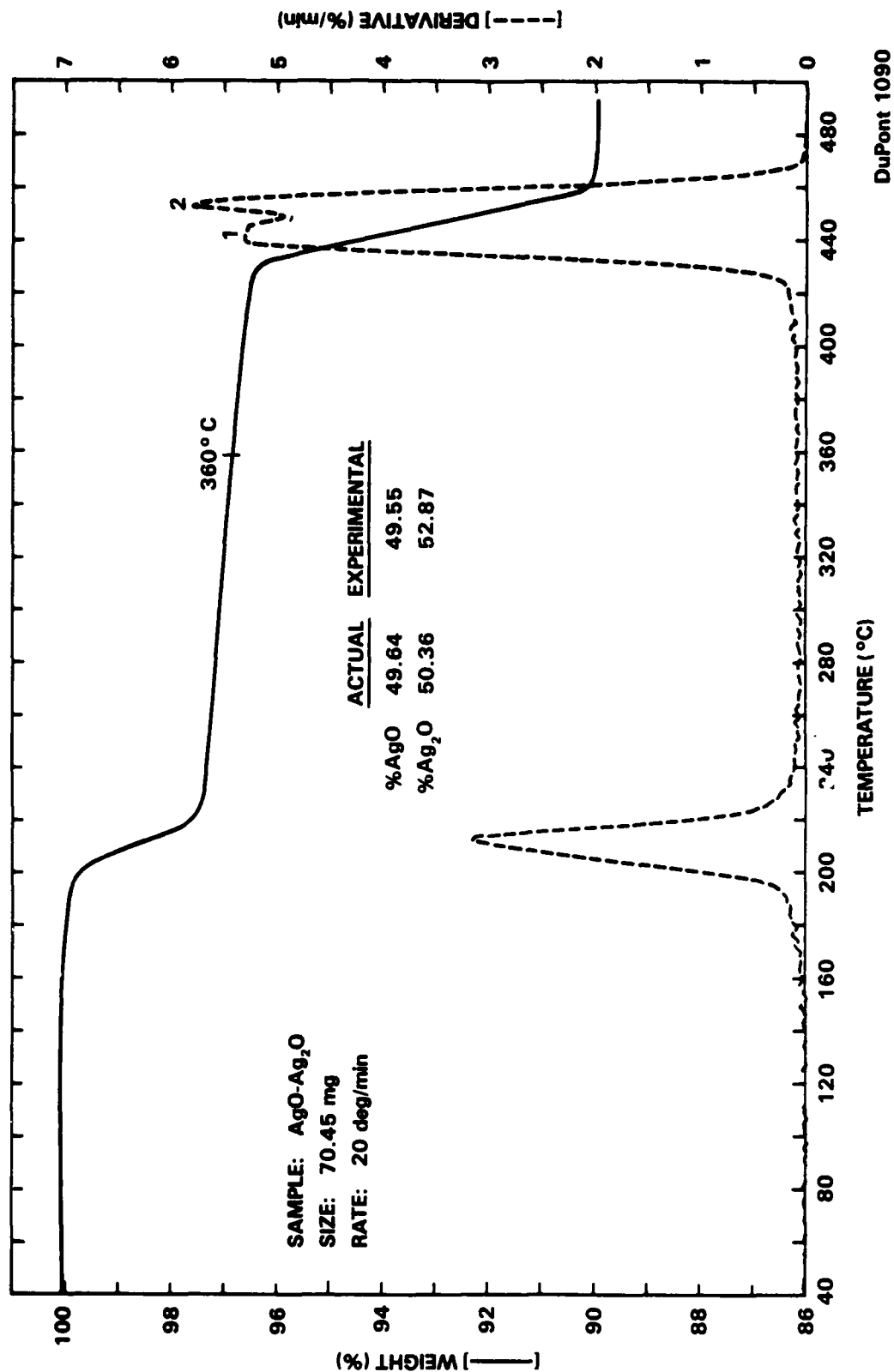


FIGURE 1. TGA CURVES OF Ag, AgO, AND Ag₂O
(A) Ag, FISHER SCIENTIFIC; (B) AgO, MMC; (C) Ag₂O, MMC

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FIGURE 2. TGA CURVE OF AgO-Ag₂O MIXTURE

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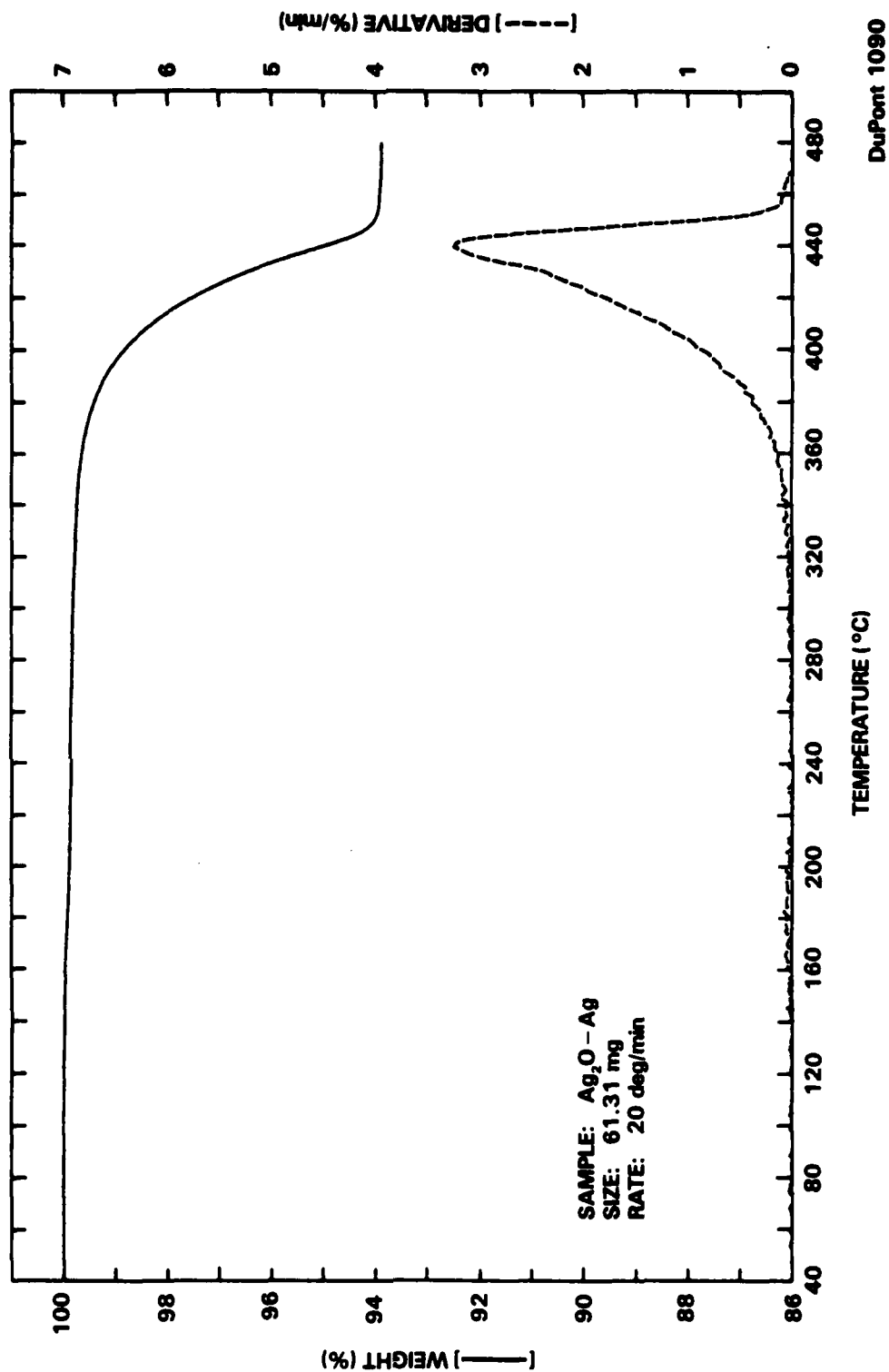


FIGURE 3. TGA CURVE OF $\text{Ag}_2\text{O}-\text{Ag}$ MIXTURE

A typical TGA curve and its derivative for a sample of active cathode material taken from a silver oxide-zinc cell are shown in Figure 4. The AgO decomposition portion of the curve has a small inflection in the area of maximum decomposition rate which is more clearly depicted on the derivative curve. The inflection was present only in cathode material samples. This small inflection is caused by the decomposition of the Ag₂CO₃ impurity present in these samples.



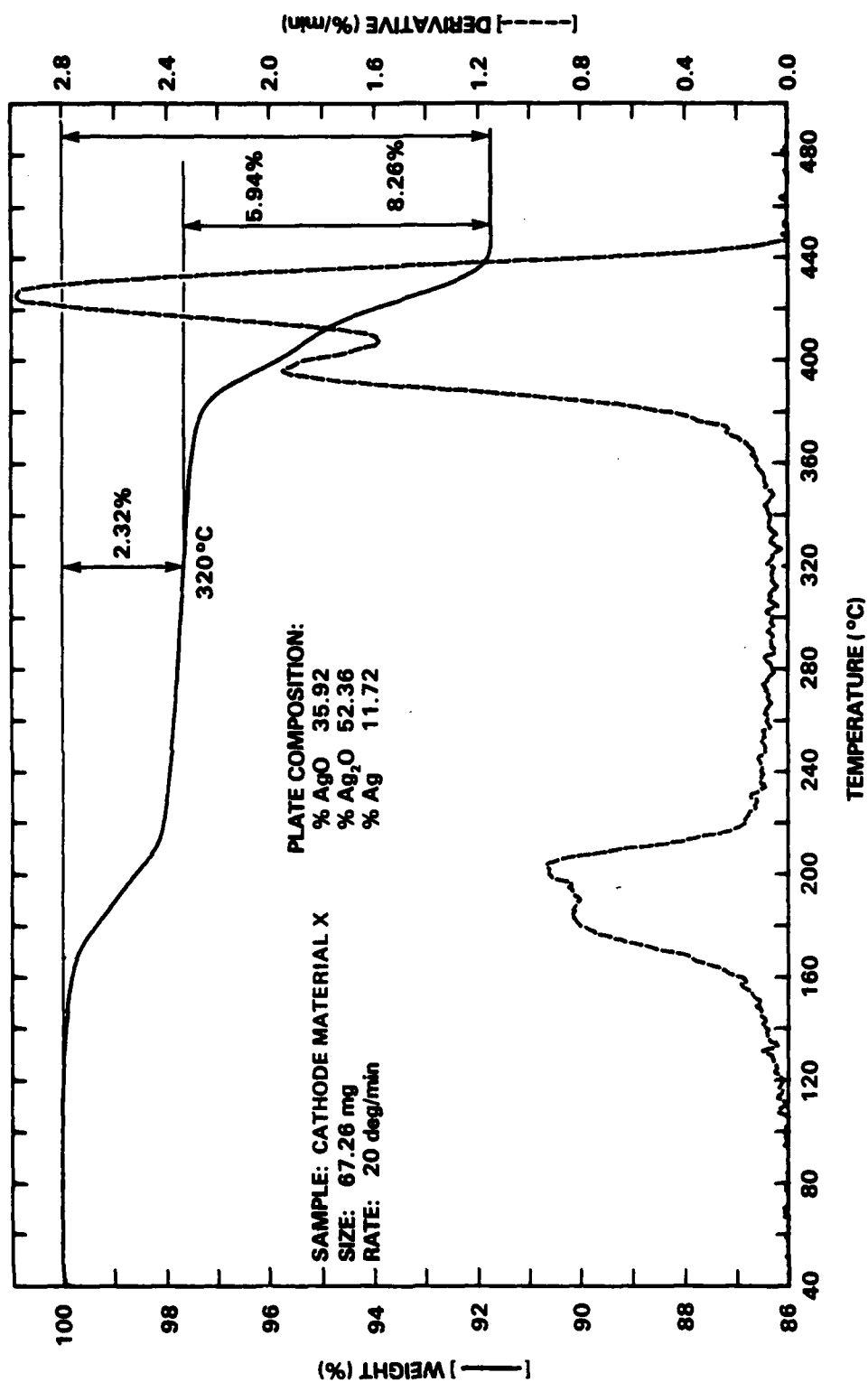
The non-horizontal plateau from about 220° to 380°C is a result of the slow, simultaneous decomposition of the two oxides in this temperature range. This continuous decomposition is also shown by the derivative curve in which there is always a measurable rate of decomposition in this range. In Figure 5, an enlargement of the derivative is shown corresponding to the non-horizontal portion of the curve. A smooth curve was drawn through this enlarged portion of the derivative; the first weight loss was then chosen at the temperature of minimum decomposition rate (320°C). The equations derived in Appendix A were then used to calculate the composition of the sample from the TGA curve (Figure 4). Because of the temperature shift of the Ag₂O decomposition portion of the curve in the presence of silver metal, the temperature of minimum decomposition rate no longer falls at 360°C, as for pure Ag₂O and AgO (Figure 1).

The precision of the method was verified by running five samples taken from a homogeneous mixture of cathode material. As seen in Figure 6, the five TGA "signatures" for the powder are almost inseparable. This is further shown in Table 1 which gives the composition of each sample and the calculated average composition.

Figure 7 shows TGA curves for silver oxide cathode materials supplied by several battery manufacturers. The wide range of compositions, as determined from the TGA curves, is a result of differences in storage conditions, age, and manufacturing processes. The figure is provided to exemplify the ease with which the AgO content of various cathode materials may be distinguished. In sample D, for example, the large initial weight loss indicates a large amount of AgO while the smaller initial weight loss for sample A indicates a much smaller amount of AgO present in the sample. The amount of AgO in a cathode is important in terms of maintaining an acceptable capacity level of a battery. Typically, chemically prepared cathode materials have much higher AgO content and better shelf lives than do electrochemically prepared cathodes;¹⁰ however, chemically prepared cathodes do not generally discharge well in high rate applications.

A limited number of experiments have been performed to determine the accuracy of the TGA method. In these tests, four samples were independently analyzed by the TGA method and by the Wagner titration method. The results of these tests are shown in Table 2.

¹⁰Bowers, F. M. and Gubner, E., "The Shelf Life of Unactivated Dry-Charged Zinc-Silver Oxide Cells," Fleischer, A. and Lander, J. J., Ed., Zinc-Silver Oxide Batteries (New York: John Wiley & Sons, Inc., 1971), pp. 347-367.



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FIGURE 4. TGA CURVE AND DERIVATIVE FOR ACTIVE CATHODE MATERIAL

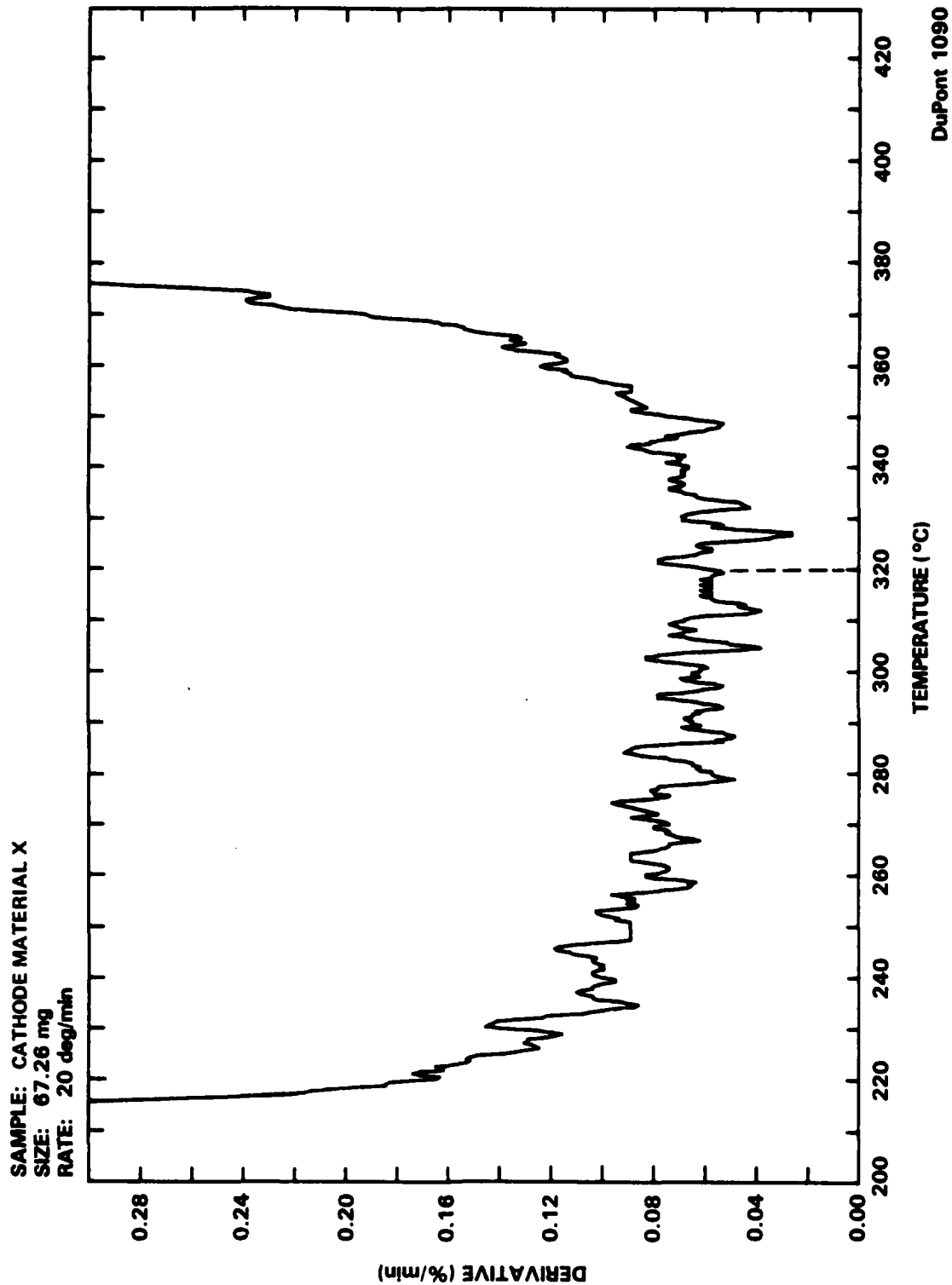
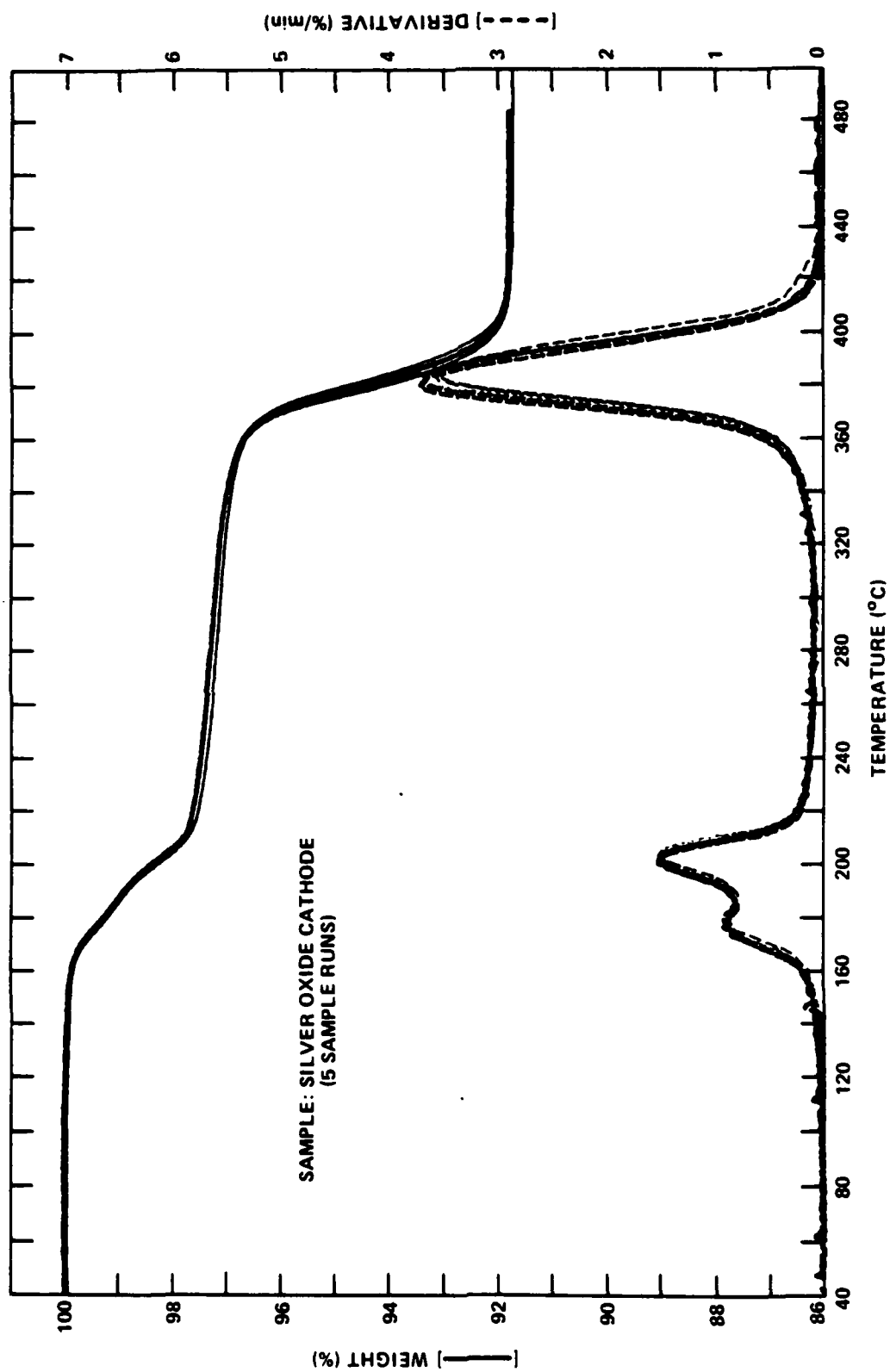


FIGURE 5. DERIVATIVE CURVE ENLARGEMENT

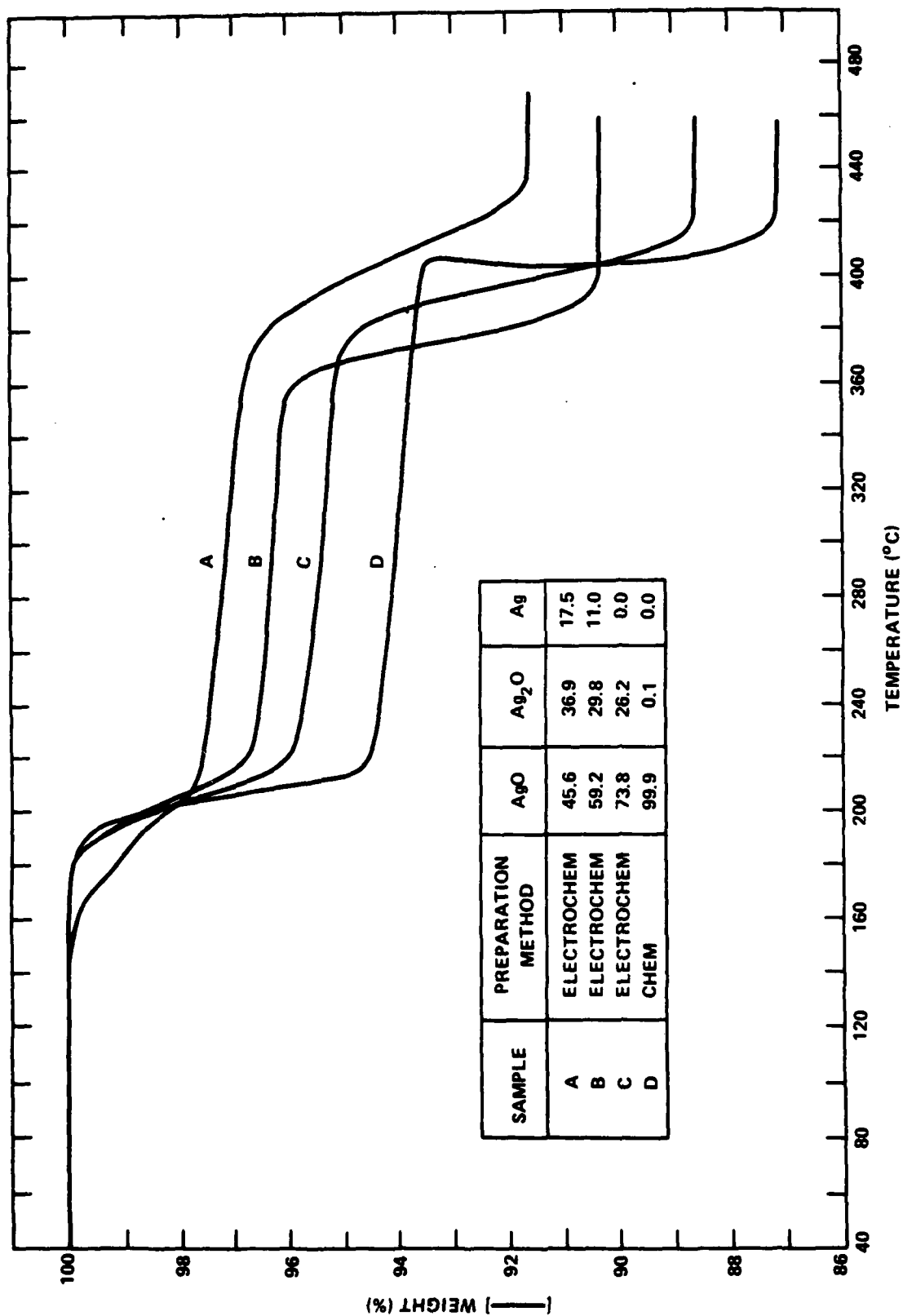


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FIGURE 6. TGA CURVES OF A HOMOGENEOUS MIXTURE OF ACTIVE CATHODE MATERIAL

TABLE 1. PRECISION OF THE TGA TECHNIQUE FOR CATHODE ANALYSIS

<u>Sample</u>	<u>% AgO</u>	<u>% Ag₂O</u>	<u>% Ag</u>
1	44.60	36.36	19.04
2	44.13	36.93	18.94
3	43.05	38.96	17.99
4	42.58	39.25	18.17
5	42.74	39.54	17.72
Average	43.42	38.21	18.37
Std. Dev.	0.90	1.46	0.59



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FIGURE 7. TGA CURVES OF VARIOUS ACTIVE CATHODE MATERIALS

TABLE 2. COMPARISON OF SILVER OXIDE ANALYSES BY TGA AND WAGNER METHODS

<u>SAMPLE</u>	<u>METHOD</u>	<u>% AgO</u>	<u>% Ag₂O</u>	<u>% Ag</u>	<u>% Ag₂CO₃</u>
W	TGA	43.28	36.07	20.65	
	WAGNER	36.68	33.82	22.48	5.64
X	TGA	43.98	40.56	15.46	
	WAGNER	41.30	34.71	18.11	4.95
Y	TGA	38.56	44.03	17.42	
	WAGNER	37.60	36.06	20.88	4.32
Z	TGA	99.92	-----	0.08	
	WAGNER	98.26	-----	0.03	1.02

Because the temperature ranges of decomposition for AgO and Ag₂CO₃ overlap, it is impossible to accurately analyze a mixture of these two substances solely by the current TGA method, especially when the latter is present at impurity levels. The correlation between the TGA and Wagner methods is best for the Ag determination. However, the AgO determination by TGA is too high because the Ag₂CO₃ determination was neglected; the mass loss from the Ag₂CO₃ decomposition (CO₂ evolution) was included in the AgO decomposition (O₂ evolution) mass loss. The Ag₂O result for TGA would be higher if the Ag₂CO₃ was accounted for, causing an even larger discrepancy between the TGA and Wagner method results. Therefore, efforts are being directed toward further development of the TGA technique to include analysis for Ag₂CO₃.

Typical DSC curves of AgO and Ag₂O samples with the corresponding TGA curves are shown in Figures 8 and 9. There is excellent agreement between the decomposition temperatures on the DSC and TGA curves, although the temperature determination of thermal transitions is inherently more accurate in DSC because of the excellent thermal contact between the sample and the thermocouple. It is seen that the decomposition of AgO is exothermic, whereas Ag₂O decomposes endothermically. In principle, the exothermic or endothermic enthalpy of a transition in DSC can be used to calculate the amount of the substance undergoing the transition. However, the measurement of mass changes in TGA is generally much more accurate than the measurement of enthalpic changes in DSC.

In Figure 10, typical DSC and TGA curves of silver oxide cathode material are shown. The effect of the carbonate impurity on these curves is clearly seen. On the TGA curve, the small inflection at about 200°C is caused by the decomposition of the Ag₂CO₃ in the same temperature range as the AgO decomposition. This is also seen as a shoulder on the AgO decomposition derivative peak. On the DSC curve, the endothermic decomposition of the Ag₂CO₃ is seen to be superimposed on the exothermic AgO decomposition peak.

Obviously, the mass loss from the evolution of CO₂ from the decomposition of the Ag₂CO₃ impurity causes an error in the determination of the silver oxide composition of the sample. Methods for analyzing Ag₂CO₃ in the presence of AgO by thermal analysis have been reported.^{11,12} We are presently developing procedures to adapt the TGA technique for determining Ag₂CO₃ at impurity levels in silver oxide cathode material.

¹¹Barnes, P. A. and Tomlinson, R. M., "The Use of DTA in the Analysis of Silver (II) Oxide for Carbonate Impurity," Journal of Thermal Analysis, Vol. 7, No. 2, 1975, pp. 469-74.

¹²Barnes, P. A. and Kirton, E., "The Development and Application of an Ultra-Sensitive Quantitative Effluent Gas Analysis Technique," Analytical Calorimetry, Vol. 3, 1974, pp. 57-67.

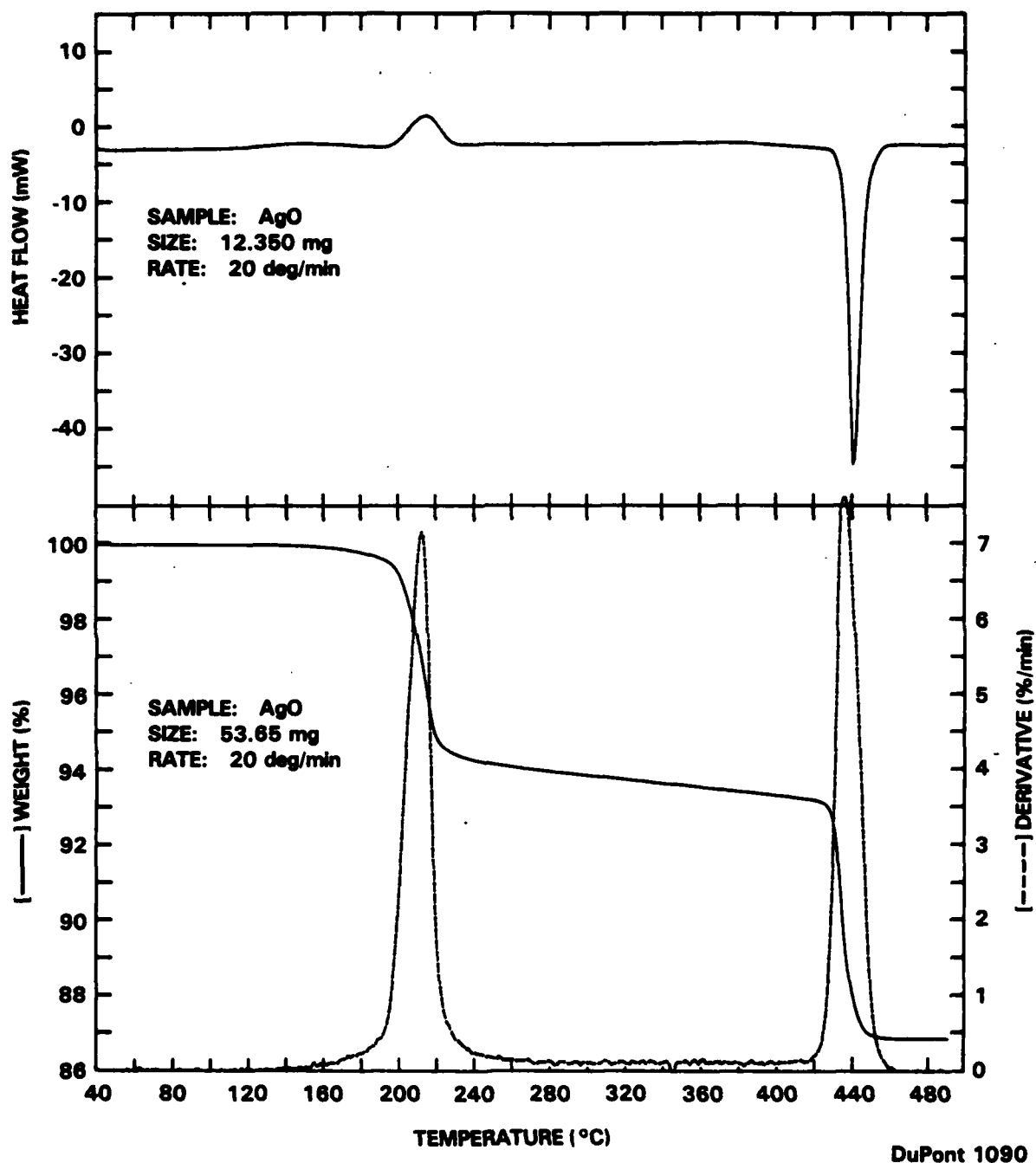
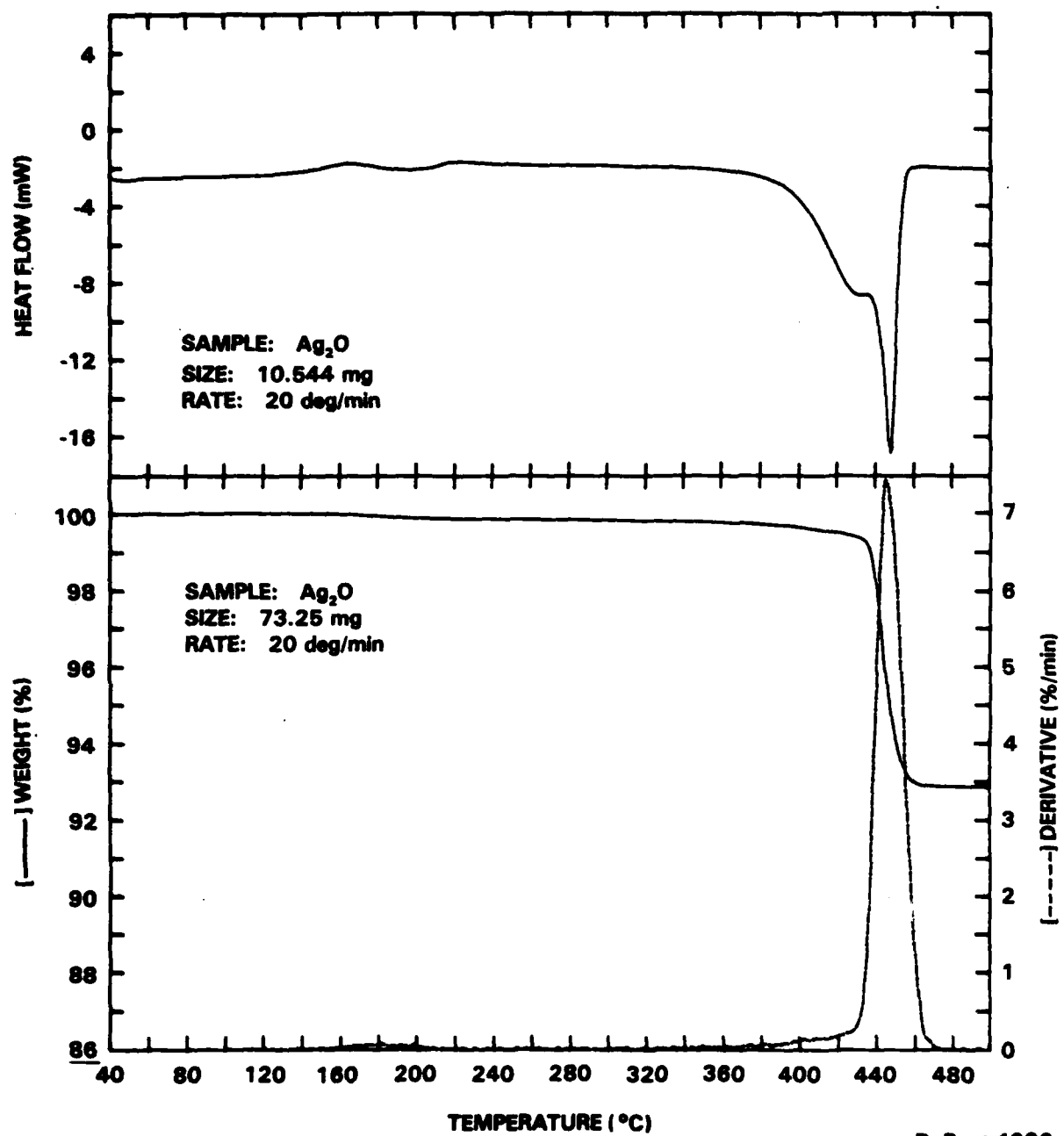
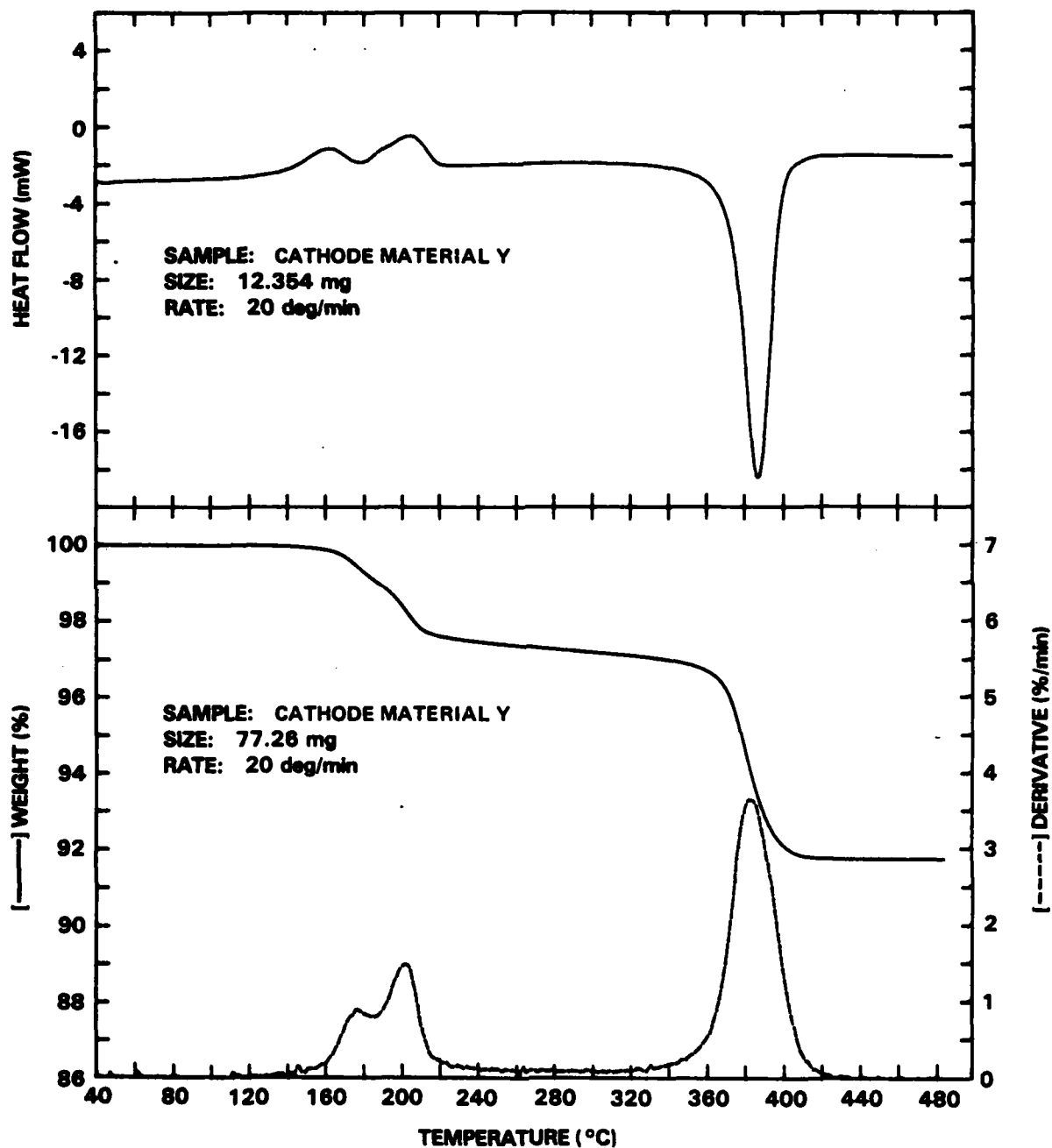


FIGURE 8. DSC AND TGA CURVES OF AgO



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FIGURE 9. DSC AND TGA CURVES OF Ag₂O



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FIGURE 10. DSC AND TGA CURVES OF CATHODE MATERIAL

CONCLUSIONS

The present study has demonstrated the utility of a newly developed, rapid and precise TGA method for analysis of mixtures of AgO , Ag_2O , and Ag as found in cathodes of silver oxide-zinc cells.

The characteristic TGA "signature" provides an extremely useful method for comparison of samples having varied histories of preparation and storage. In addition, after further work to establish the accuracy of the method, this technique may be suitable for use as a quality control tool where active cathode material composition limits may be imposed during manufacture of cathode plates or powder.

A method for the simultaneous determination of carbonate impurity in silver oxide samples, using the new TGA technique, is presently under investigation.

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2. Wagner, R. D., A Method for the Quantitative Analysis of the Silver Oxide Cathode, NOL TR 64-214, Aug 1965.
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11. Barnes, P. A. and Tomlinson, R. M., "The Use of DTA in the Analysis of Silver (II) Oxide for Carbonate Impurity," Journal of Thermal Analysis, Vol. 7, No. 2, 1975, pp. 469-74.
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APPENDIX A

DERIVATION OF EQUATIONS RELATING COMPOSITION OF AgO,
Ag₂O, Ag MIXTURES TO THE TGA CURVE

Mixtures of solids which decompose to form volatile products may be conveniently analyzed by the TGA technique, provided the decomposition of each component occurs at a different temperature. The resulting TGA curves can be analyzed using a set of simultaneous equations which describe each decomposition process. Figure A-1 gives a theoretical TGA curve for mixtures of silver metal and the silver oxides. Using the curve, variables may be defined and the set of simultaneous equations derived. The solution to these equations provides the relationship between the TGA curve and the components in the original sample.

Three assumptions were made in the derivation of the equations. First, each oxide must be stoichiometric in composition. Second, the mass loss associated with the decomposition of either oxide is directly proportional to the amount of the oxide in the original sample; however, the proportionality constants differ for the two oxides. Finally, the only components in the mixture are AgO, Ag₂O, and Ag. Using these assumptions, the derivation of the relationship between weight loss upon decomposition of the mixture and its initial composition can be made.

Based on the decomposition reactions (1) and (2), two equations may be written to describe the weight loss associated with each component.



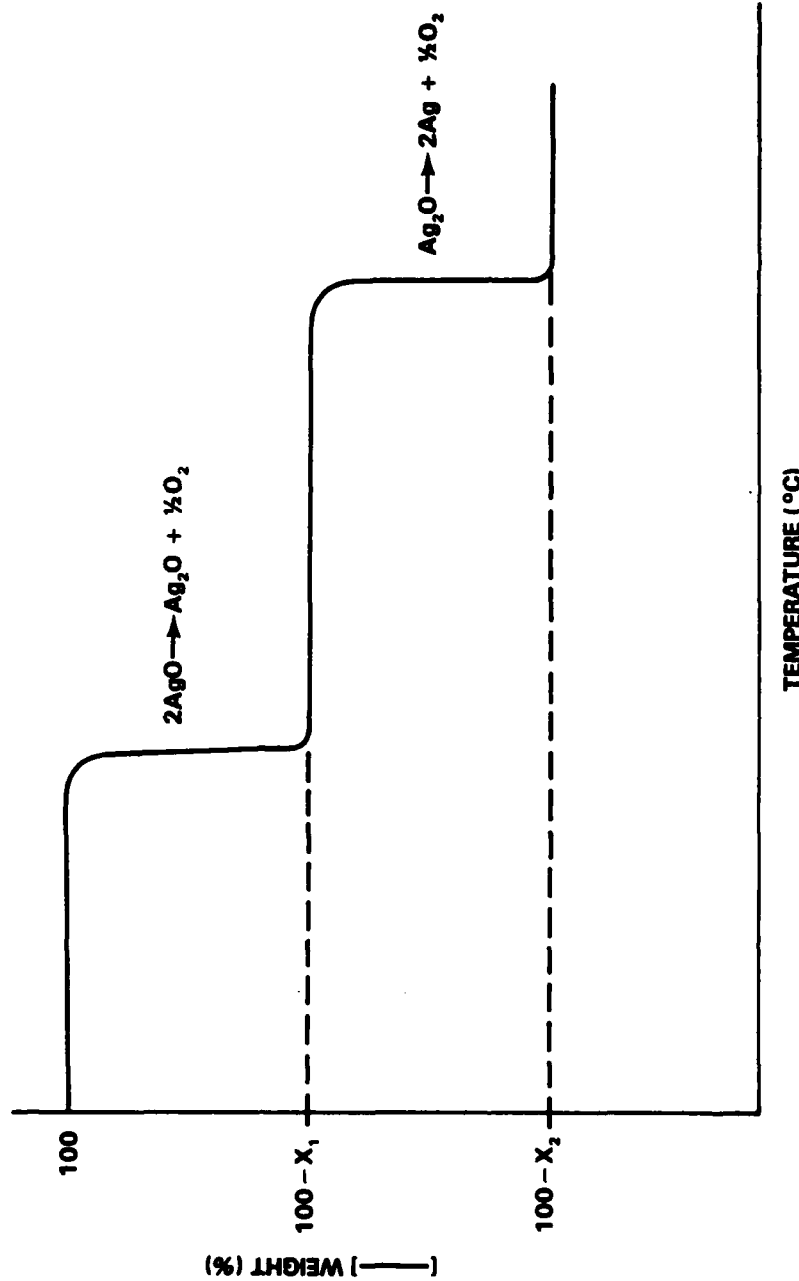
The oxygen loss associated with the decomposition of AgO is defined as ΔW_1 and is represented as

$$\Delta W_1 = \frac{M_{\text{O}}}{2M_{\text{AgO}}} W_{\text{AgO}} \quad (\text{A-3})$$

where M_{O} is the atomic weight of oxygen, M_{AgO} is the molecular weight of AgO and W_{AgO} is the mass of AgO in the sample. Substituting the known values of M_{O} and M_{AgO} ,

$$\Delta W_1 = 0.06458 W_{\text{AgO}} \quad (\text{A-4})$$

The second mass loss, ΔW_2 , results from the decomposition of Ag₂O. There are two sources of Ag₂O in the sample. The first source of Ag₂O is simply the



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FIGURE A-1. THEORETICAL TGA CURVE FOR MIXTURES OF AgO, Ag₂O, AND Ag

Ag₂O initially present in the sample; the second source is from the decomposition of AgO. Thus, the value of ΔW_2 has two components and may be written as:

$$\Delta W_2 = \frac{M_O}{2M_{AgO}} W_{AgO} + \frac{M_O}{M_{Ag_2O}} W_{Ag_2O} \quad (A-5)$$

where M_{Ag_2O} is the molecular weight of Ag₂O and W_{Ag_2O} is the mass of Ag₂O initially in the sample. Substituting again for M_O , M_{AgO} , and M_{Ag_2O} :

$$\Delta W_2 = 0.06458 W_{AgO} + 0.06904 W_{Ag_2O} \quad (A-6)$$

The total mass loss, ΔW , is then given by the sum of ΔW_1 and ΔW_2 :

$$\begin{aligned} \Delta W &= \Delta W_1 + \Delta W_2 \\ \Delta W &= 0.12916 W_{AgO} + 0.06904 W_{Ag_2O} \end{aligned} \quad (A-7)$$

Converting to percentages and letting X_1 equal the percent of the first weight loss and X_2 equal the percent of the total weight loss, the percent composition of the cathode material may be given as follows:

$$\begin{aligned} X_1 &= 0.06458 (\% AgO) \text{ or} \\ \% AgO &= 15.485 X_1, \end{aligned} \quad (A-8)$$

$$\begin{aligned} X_2 &= 0.12916 (\% AgO) + 0.06904 (\% Ag_2O) \text{ or} \\ \% Ag_2O &= 14.484 (X_2 - 2X_1), \text{ and} \end{aligned} \quad (A-9)$$

$$\% Ag = 100 - (\% AgO + \% Ag_2O). \quad (A-10)$$

Note that the percent silver metal is determined by difference.

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