

KH-69-20 DRY CHLORINATION STUDIES OF CPC By: R. C. Lutton 12/69

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E. I. DU PONT DE NEMOURS & COMPANY

Pigments Department

Newport Plant

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NEWPORT PLANT

PIGMENT COLOR RESEARCH REPORT

DRY CHLORINATION STUDIES OF CPC

SERIAL NO.: KN-69-20

Date: 12/69

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SUBJECT: DRY CHLORINATION STUDIES OF CPC

SUBMITTED BY: R. C. LUTTON

APPROVED BY: J. F. MAURER DATE ISSUED: 12/69

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DRY CHLORINATION STUDIES OF CPC

I. SUMMARY

The dry chlorination of CPC blue crude in the presence of AlCl_3 has been studied. A 1-liter agitated pot reactor was used with Cl_2 gas fed through a dry mixture of CPC, AlCl_3 , NaCl , and in some cases a diluent sand. Most of the runs were conducted at 300°C . The amount of AlCl_3 was varied, but in all cases it was less than half than that of the eutectic melt process. Samples of the product were taken at various time intervals from as low as one hour up to 18 hours.

The samples were analyzed first for percent purity of CPC by leaching with a mixed-solvents technique and second for organic chloride by Parr bomb fusion followed by Volhard titration. Dry rubouts were also made of the samples to give a qualitative check of the analyses.

The quantitative analyses in the salt diluent runs are inconsistent and do not seem to correlate with the colors of the dry rubouts. Thus while the dry rubouts indicate a definite advantageous effect of the AlCl_3 - NaCl , no conclusions can be drawn from the quantitative analysis.

I believe the proposed process warrants further study, but only after the quantitative analysis and the dry rubouts can be investigated and the differences explained or eliminated.

II. INTRODUCTION

The purpose of this research was to study a possible process for the chlorination of CPC, copper phthalocyanine (blue to green).

The present Newport plant process is a reaction with sulfur dichloride under pressure. In a proposed expansion alternate chlorination processes are being considered, namely the eutectic melt process used by Orchem and a dry chlorination process. It is this latter which was studied in the present research.

Some work had been done with dry chlorination using fluidized beds of CPC and salt (1, 2, 3). Temperatures were in the range 200 - 400°C . and the process seemed promising up through the semiworks stage. At that point, however, development work was dropped and has been inactive for 20 years.

It was felt that the dry chlorination process should be examined using the AlCl_3 as a catalyst-complexing agent with possible better quality and lower temperatures than were possible in the previous work. The role of AlCl_3 in the present SCl_2 process and the eutectic melt process (both liquid phase reactions) has been established. The question is whether this same enhancing of chlorination will be accomplished in the proposed gas-solid chlorination at substantially lower concentrations of AlCl_3 ($\text{AlCl}_3:\text{CPC}$). Unless this process can be carried out at lower AlCl_3 , then it probably will not be any better than the eutectic-melt process.

III. APPARATUS AND PROCEDURE

The reactants were premilled in two different manners. In the early runs where large amounts of reactant were required, a ball mill with cyl pebs and roofing nails was employed. In the later runs using only one-tenth the reactants with sand diluent the charge was prepared by mortar and pestle in a glove-bag.

The chlorination was carried out in a 1-liter Pyrex resin flask with four tapered outlets in the cap. Temperatures up to 375°C . were obtainable with a 335-watt heating mantle. A Tri-R Stir-R Model K-43 was used to drive an Inconel stirrer with helical blades. The speed was not measured but the setting was 3 on a range 0-10 for a rating 50-1100 rpm. This produced effective mixing in most cases except when sand was used as a diluent which settled to the bottom. This effect was advantageous as it kept the reactants up in the region of best agitation and higher chlorine concentration. Temperature was determined by thermocouples at two depths on the inner wall of the flask and was shown on a recorder. Chlorine was fed through copper tubing to a point above the stirrer blades but below the reactant level. The exit gases were to pass off through a NaOH solution bubbler, but instead vented around the stirring shaft seal.

Most of the runs were isothermal and controlled manually. The reactants were heated and agitated, and when the required temperature had been achieved, the chlorine gas was introduced and the timed run begun. Two or three times during a run the reaction was interrupted and cooled to take a sample. The flask was then reheated and the run restarted with introduction of chlorine.

Three temperature levels were investigated but most of the runs were at 300°C. Three levels of chlorine flow rate were used ranging from a stoichiometric rate equivalent to about 1 Cl atom per CPC molecule per hour up to about 1 Cl atom per CPC molecule per 4.4 minutes. Four levels of AlCl₃-NaCl eutectic in the reactants were used; namely CPC:eutectic ratios of 1:0, 1:0.5, 1:1, 1:2. Time did not permit a complete sequence of all variables at all levels, nor was there an attempt to statistically design the sequence. Rather the areas were investigated on the basis of sequential decisions.

The samples were analyzed first for percent purity of CPC by leaching with a mixed-solvents technique and second for organic chloride by Parr bomb fusion, followed by Volhard titration.

The reactants used in the experimental runs were:

CPC Blue Crude (Lot #1378, 6/13/69, Newport)

AlCl₃ (plant process chemical)

NaCl (plant process chemical)

A Differential Thermal Analysis technique was developed by J. E. Johnson to determine qualitatively the effect of temperature, reactant composition and gas flow rate on the rate and extent of reaction. By this means, it was hoped to screen the range of variables and thus concentrate the effort upon a narrow range, using the more involved agitated-pot reactor.

The details of the DTA study are included in the appendix of this report.

IV. RESULTS

The yield as percentage chlorine in the CPC was shown to be a function of reaction time with parameters of chlorine flow rate, temperature and reactant composition. The following table shows the relationship.

TABLE I

RESULTS OF CHLORINATION RUN

Run No.	Temperature °C.	Cl ₂ Flow Rate cc/min.	Weight Ratio CPC:Eutectic	Weight Ratio Reactants:Diluent Sand	Time Hrs.	% Purity (CPCx100) Reactants	% Cl in CPC
1	25 + 200	60--100	1:1	200g:0	2.35	47.33	4.60
2	200	60--100	1:1	200g:0	6.0	45.98	9.90
3	200 + 350	60--100	1:1	200g:0	2.92	55.61	29.32
4	300	60--100	1:1	200g:0	6.00	59.60	41.47
4a	↓	↓	↓	↓	12.50	51.35	46.89
4b	↓	↓	↓	↓	18.08	48.36	46.05
5a	350	60--100	1:0*	200g:0	4.83	61.31	43.30
5b	↓	↓	↓	↓	10.83	76.61	53.07
5c	↓	↓	↓	↓	17.83	78.99	54.25
6a	300	169	1:1	200g:0	1.0	51.99	14.85
6b	↓	↓	↓	↓	2.0	56.97	29.07
6c	↓	↓	↓	↓	3.0	60.98	33.82
7a	300	169	1:1	20g:454g	1.0	9.13	9.13
7b	↓	↓	↓	↓	3.0	11.47	11.47
8a	300	83.	1:1	20g:454g.	1.0	2.24	2.24
8b	↓	↓	↓	↓	3.0	30.67	30.67
8c	↓	↓	↓	↓	4.0	8.35	8.35
9a	300	169	2:1	20g:454g	1.0	4.53	4.53
9b	↓	↓	↓	↓	3.0	20.60	20.60
10a	300	169	1:2	20g:454g.	1.0	1.75	1.75
10b	↓	↓	↓	↓	5.0	0.59	0.59
11a	300	169	1:0*	20g:454g.	1.0	2.24	2.24
11b	↓	↓	↓	↓	5.0	8.27	8.27

* In Runs 5 and 11, no AlCl₃ was used but CPC:NaCl= 1:3

VI. DISCUSSION OF RESULTS

In the first three runs the effect of reaction temperature was investigated at an arbitrarily selected reactant ratio and chlorine flow rate. At 200°C. and lower the reaction was too slow to yield any useful information in this particular reactor. At a temperature of 375°C. the reactants formed a hard cinder and jammed the agitator. For these reasons most of the runs were at 300°C.

In the first six runs the charge consisted of 200 g. of which 100 g. was CPC, except in Run 5 with 50 g. CPC. With this much CPC and the 60-100cc/min. chlorine flow rate used in Runs 1-5, the maximum possible chlorination rate was approximately 1 to 2 Cl atom per CPC molecule per hour. Indeed this seems to be a maximum rate that some, but not all of the runs, approach.

The analysis for percent chlorine for Run 5 is apparently in error since the 53.07% and 54.25% Cl in CPC is higher than 16 Cl atoms per molecule. Also, a blank on the unchlorinated reactants analyzed 37.6% rather than the expected 0%. This in combination with the impossibly high percent purity in Run 5 indicates that some NaCl may not have been leached out by the mixed solvents and was assayed as CPC.

Further evidence of the invalidity of the analysis of Run 5 is provided by a dry rubout of the products. While admittedly qualitative there is nevertheless a reasonable correlation between the color change from blue to green with a percent Cl of 0 to 47. However, in Run 5 the rubout colors look more like 10%, 20%, 30% (all +10%) rather than 43.3%, 53.07% and 54.25%.

In Runs 7-11 the amount of CPC per charge was decreased to 10g and this equivalent increase in stoichiometric proportion of chlorine should have reflected an equal or greater reaction rate. The analytical results, however, are generally low and inconsistent with the qualitative results of the dry rubout of the products. It appears as though the presence of the sand somehow adversely affects the quantitative analysis.

VII. CONCLUSIONS

It is impossible to draw any conclusions regarding the effect of aluminum chloride from the analytical data.

However, within the reliability of the dry rubout technique it certainly appears that dry chlorination of CPC is markedly facilitated by the presence of AlCl_3 -NaCl eutectic. Over the range of concentration studied the lower the ratio CPC:eutectic the greener the product.

VIII. RECOMMENDATIONS

1. The process of dry chlorination of CPC in the presence of AlCl_3 should be investigated further, but only after a consistent analytical process for chlorine in CPC has been developed.

Appendix



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INCORPORATED

WILMINGTON, DELAWARE 19898

ENGINEERING DEPARTMENT

August 7, 1969

R. LUTTON
PIGMENTS DEPARTMENT
NEWPORT PLANT

ENGINEERING TEST CENTER
THERMAL ANALYSIS OF CPC CHLORINATION

Differential Thermal Analysis (DTA) has been used in this brief study to correlate several compositions and milling preparations with the type of exothermic chlorination indicated by DTA. No assays of the small samples (10-50 mg) were made, but green material resulted from all chlorination runs.

We have concluded the following:

- The method is not highly quantitative or reproducible due to the following equipment limitations:
 - Lack of room in the sample tube for the standard ceramic thermocouple centering sleeve because of the chlorine feed tube.
 - Plugging of the chlorine feed tube. This was partially corrected by using a 1/4" tapered point instead of a blunt end.
- The chlorination for all samples occurs across very broad temperature regions in the range 125-375°C at a scanning rate of 20°C/minute. Neither lower rates nor time-base studies were included.
- Exothermic indications were observed on samples containing no sodium chloride or aluminum chloride (see Run 7, T-2).
- The ball-milled samples (T-1 and T-5) appear to begin the exothermic reaction at a lower temperature than the hand-milled samples.

APPENDIX A-2

2

August 7, 1969
R. Lutton

- Aluminum chloride sublimes beginning at about 40°C (see Run 12, T-7).
- A small, low-temperature (52°C) endothermic indication of unknown type was observed on one DTA run at high resolution (Run 13, T-7).

EXPERIMENTAL NOTES

Chlorine was fed directly to the bottom of the glass capillary tube used for DTA. The metal thermal shield and glass bell jar were not used, and a 4" vent hose was mounted directly over the silver furnace block for rapid removal of the excess reactive chlorine. One result of the draft was large heat losses, so that the scanning may have decreased at the highest temperatures in spite of maximum driving voltage.

SUGGESTIONS FOR FURTHER WORK

Improvements in the positioning and securing of the thermocouple and chlorine feed tube should result in greater reproducibility.

Microanalysis of the products for pigment assay might be possible. One difficulty will be removal of the soluble chlorides with such small samples.

Isothermal time studies to show the duration of the reaction could be made.

ENGINEERING SERVICE DIVISION
Engineering Test Center

James E. Johnston

J. E. Johnston

JEJ:lsr
Attachment

APPENDIX A-3

3.1 SYSTEM DESCRIPTION

The DTA system is shown schematically in Figure 3C. S and R represent the thermocouple junctions of the system immersed in sample and reference respectively. The thermocouple common sides are joined at B. The difference in temperature between sample and reference, ΔT , is indicated by the electrical potential across the points A-C.

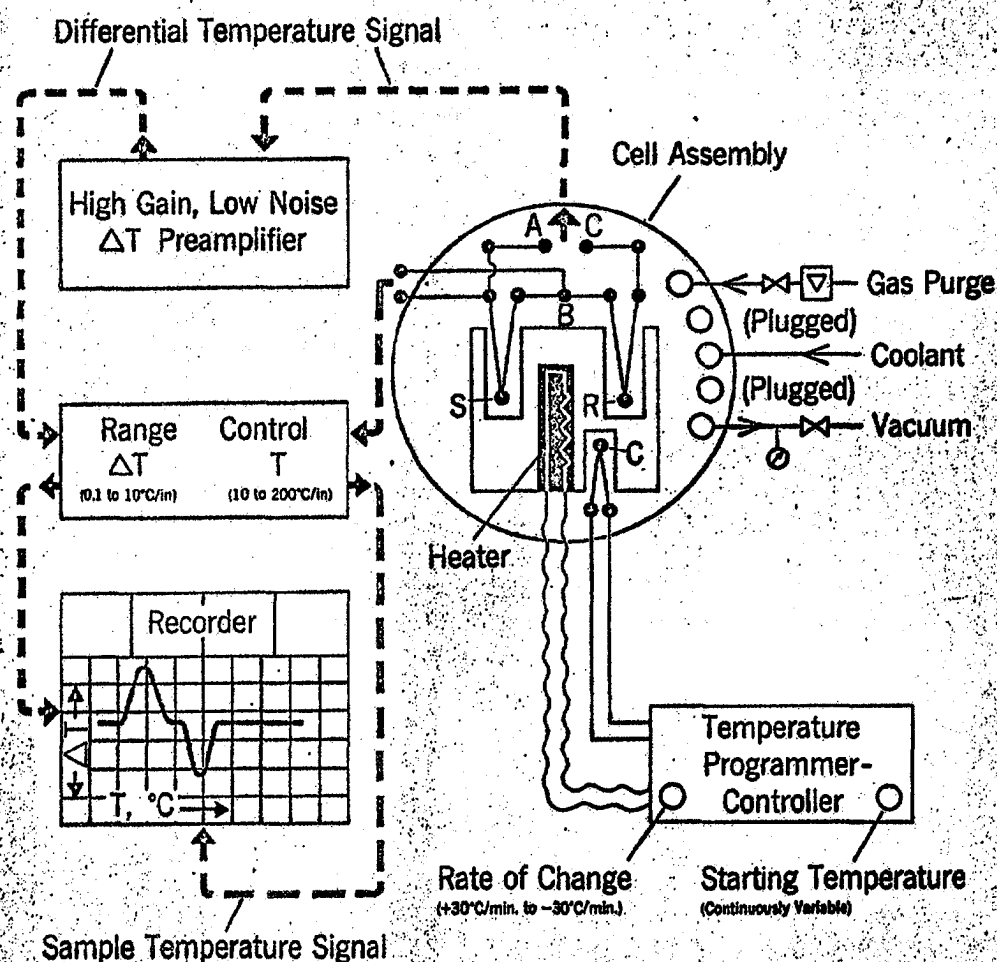


FIGURE 3C ANALYZER SYSTEM

APPENDIX A-4

CPC CHLORINATION BY THERMAL ANALYSIS

SAMPLE LIST

<u>SAMPLE</u>	<u>WEIGHT % COMPOSITION</u>			<u>NOTES</u>
	<u>CPC</u>	<u>NaCl</u>	<u>AlCl₃</u>	
T-2	100	0	0	Un-milled, crude, "Lot 1378, 6/13/69", kerosene = 1/2% maximum
T-1	25	75	0	Ball-milled, 7 hours
T-3	50	7.9	42.1	Ball-milled. Discarded due to CPC losses found in mill
T-4	50	7.9	42.1	Hand-milled 10 minutes, mortar and pestle
T-5	50	7.9	42.1	Ball-milled, 7 hours
T-6	66.7	5.3	28	Hand-milled
T-7	33.3	10.5	56.2	Hand-milled

JEJ:lsr
8/6/69

APPENDIX A-5

CPC CHLORINATION BY THERMAL ANALYSIS

EQUIPMENT LIST

Differential Thermal
Analyzer

Model 900
Standard Cell
Macro Tubes
(3 MM ID)

E. I. du Pont de Nemours & Co.
Instrument Products Division
Wilmington, Delaware 19898

Chlorine Feed Tubes

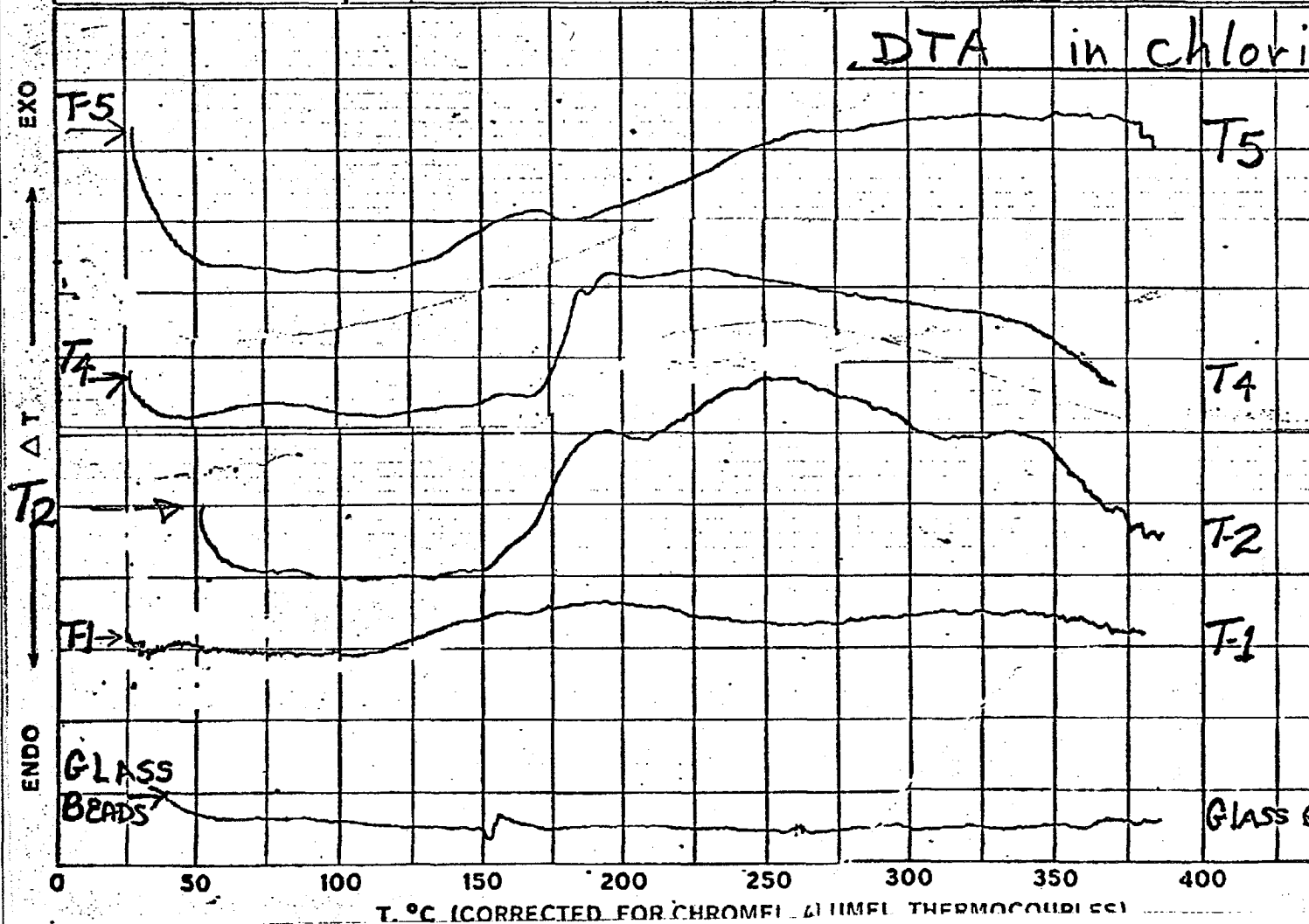
.058" OD x
.043" ID
stainless steel
hypodermic
tubing,
No. 383175

Du Pont Experimental Station
Stores

Gas Flowmeters

Brooks Sho-Rate
Rotameter
Tube R-2-15-AAA
Sapphire float
0-77 cc/min air
0-43.5 cc/min
chlorine

SAMPLE: T-1 = 42.9mg T-4 = 40.85mg T-2 = 15.35mg T-5 = 41.44mg ORIGIN: R. Lutton / Newport		SIZE AS NOTED 4 REF. GLASS BEADS 1/2 6cc/min PROGRAM MODE Heat RATE 20 °C	ATM. C_{12} 8.70 cc/min T SCALE SETTING 50 * 5.0 * Std DTA cell / Macco tubes	RUN NO. DATE 7-28 OPERATOR H
---	--	--	--	------------------------------------



SAMPLE: CPC-NaCl-AlCl₃

SIZE $\frac{1}{4}$ " in macro tubes (4 min)

ATM. Chlorine, 8.7 cc/min

REF. Same, Na, 6 cc/min

PROGRAM MODE Heat

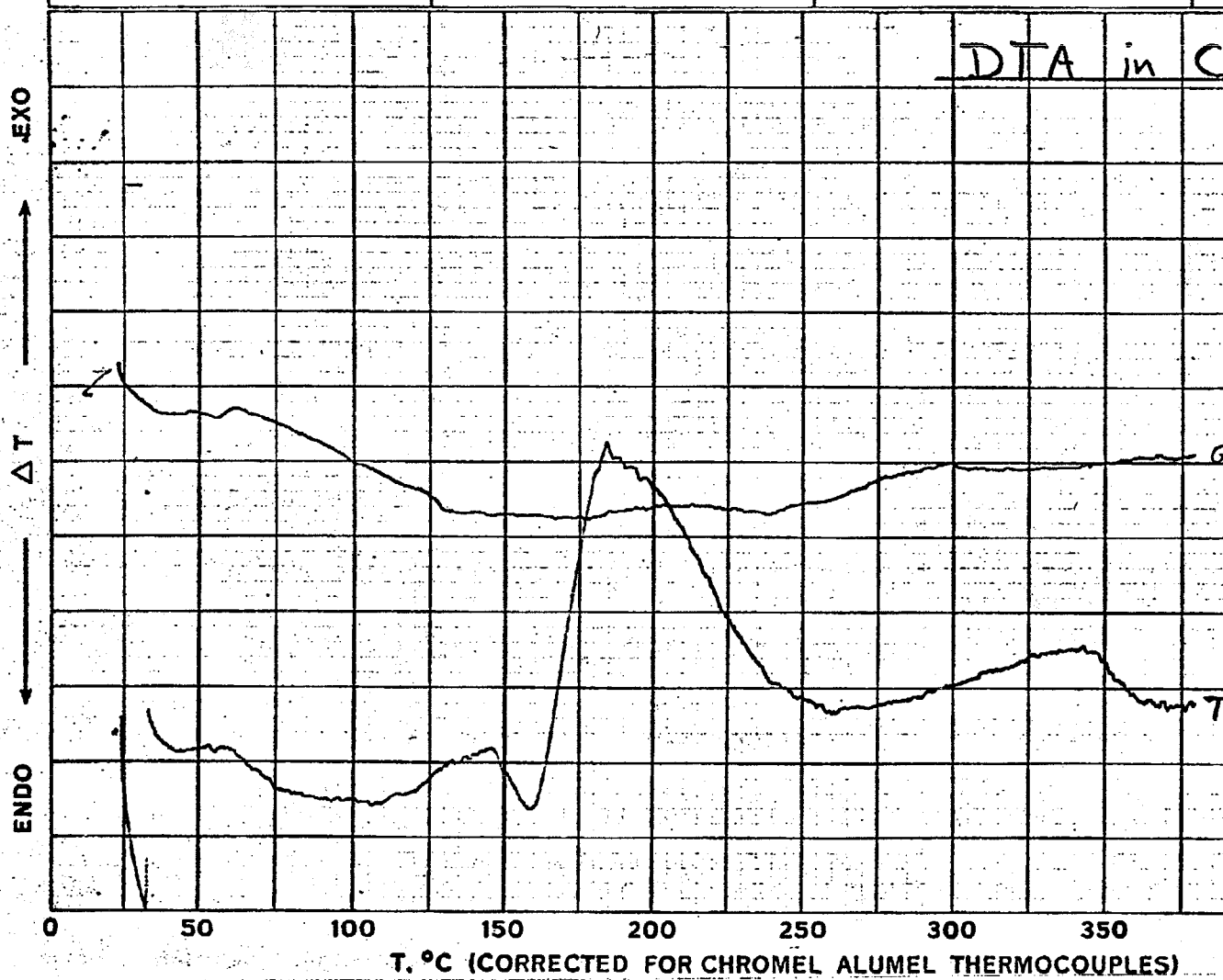
	T	ΔT
SCALE	50	2

ORIGIN: R. Lutton, Newport

RATE 20 $\frac{^\circ\text{C}}{\text{min}}$ START $^\circ\text{C}$

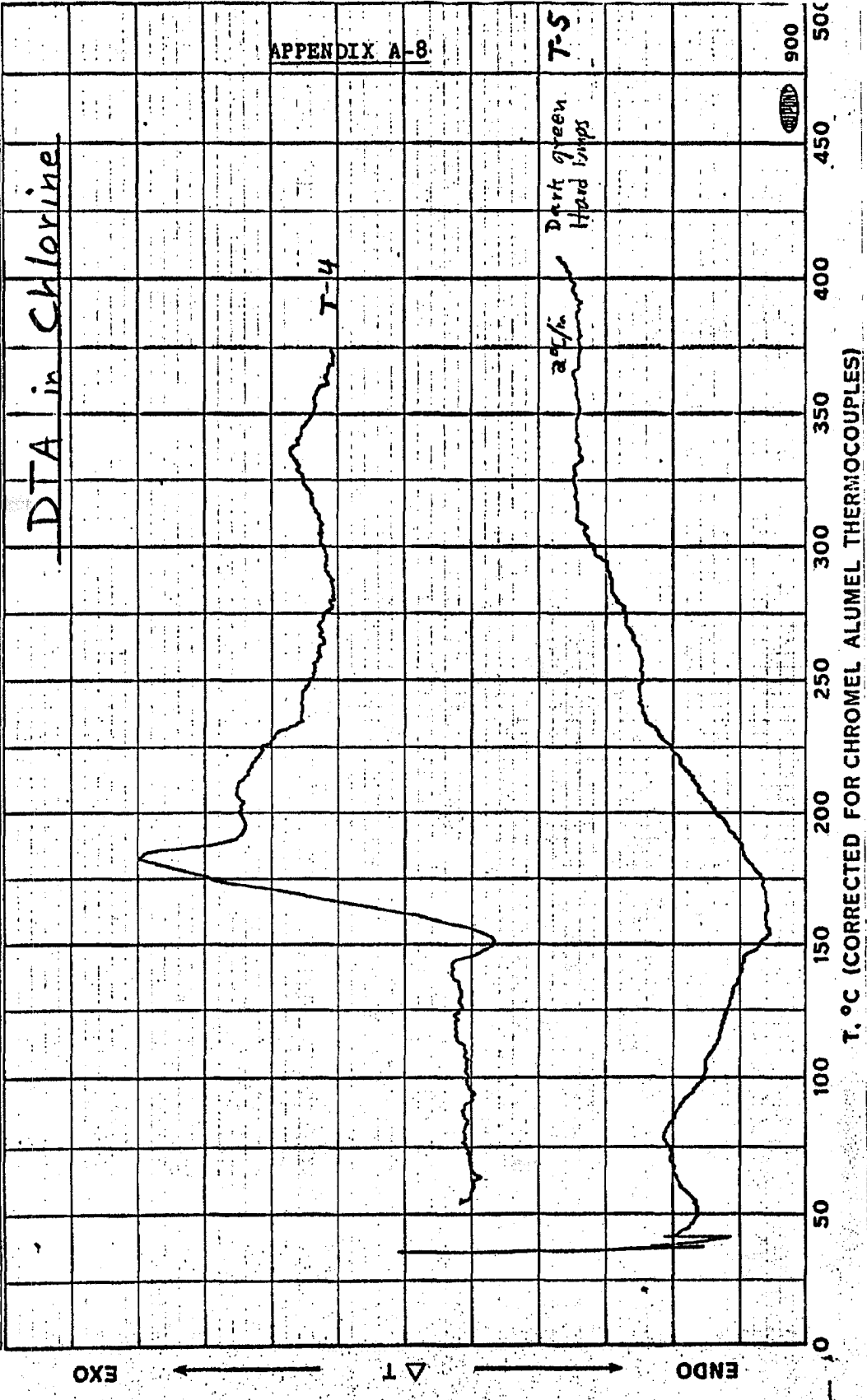
SETTING

Std. DTA Cell



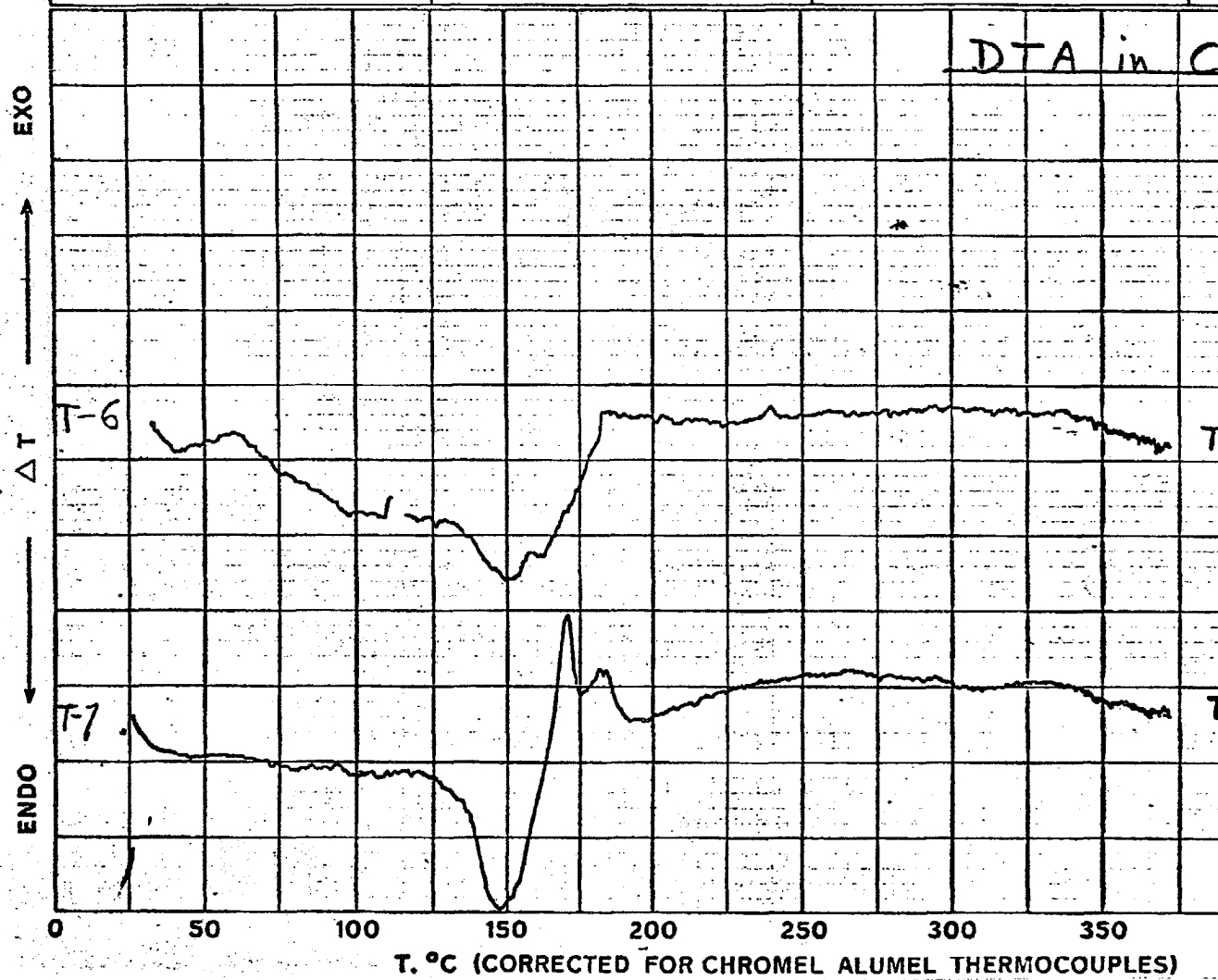
T. °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

SAMPLE: CPC-NaCl-AlCl ₃	SIZE $\frac{1}{4}$ " in Inactive tubes	ATM. Chlorine, 8.2 cc/min	RUN NO. 6
	REF.	T ΔT	DATE 7/25/69
ORIGIN: R. Lottan, Newport	PROGRAM MODE Heat	SCALE 50 $\frac{\Delta T}{\text{in}}$	OPERATOR J. C. Johnston
	RATE 20 $\frac{\text{in}}{\text{min}}$, START $^{\circ}\text{C}$	SETTING 2 $\frac{\text{in}}{\text{min}}$	

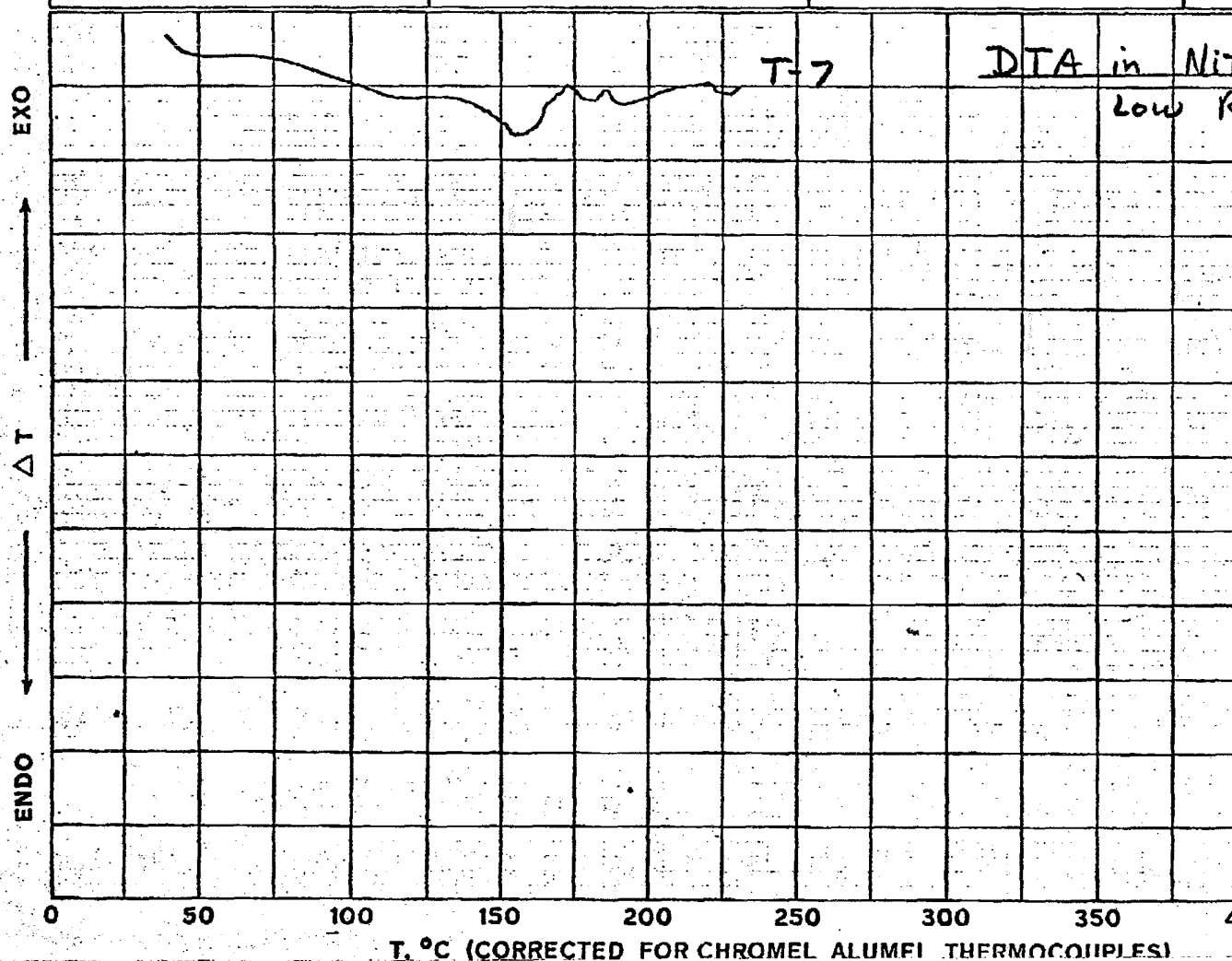


.20811 .21057
.00812 .00333

SAMPLE: T-7 T-6	SIZE	ATM. Cl_2 , 8.7 cc/min
	REF. T-7, N_2	
ORIGIN:	PROGRAM MODE Heat	SCALE SETTING
	RATE 20 $\frac{^\circ C}{min}$ START $^\circ C$	50 $\frac{^\circ C}{min}$ 2 $\frac{^\circ C}{min}$



SAMPLE: <u>T-7</u> Re-evacuated ORIGIN:	SIZE <u>1/8" depth in tube</u>	ATM. <u>O₂-free N₂, no flow</u>		RUN
	REF. <u>Glass beads</u>	T	ΔT	DATE
	PROGRAM MODE <u>Heat</u>	SCALE <u>50</u>	<u>2</u>	OPER
	RATE <u>20</u> $\frac{^\circ\text{C}}{\text{min}}$, START <u> </u> $^\circ\text{C}$	SETTING <u>Standard Cell</u>		



SAMPLE: T-7

Pre-evacuated
ORIGIN:

SIZE $\frac{1}{8}$ " depth in tube

REF. Glass Beads

PROGRAM MODE Heat

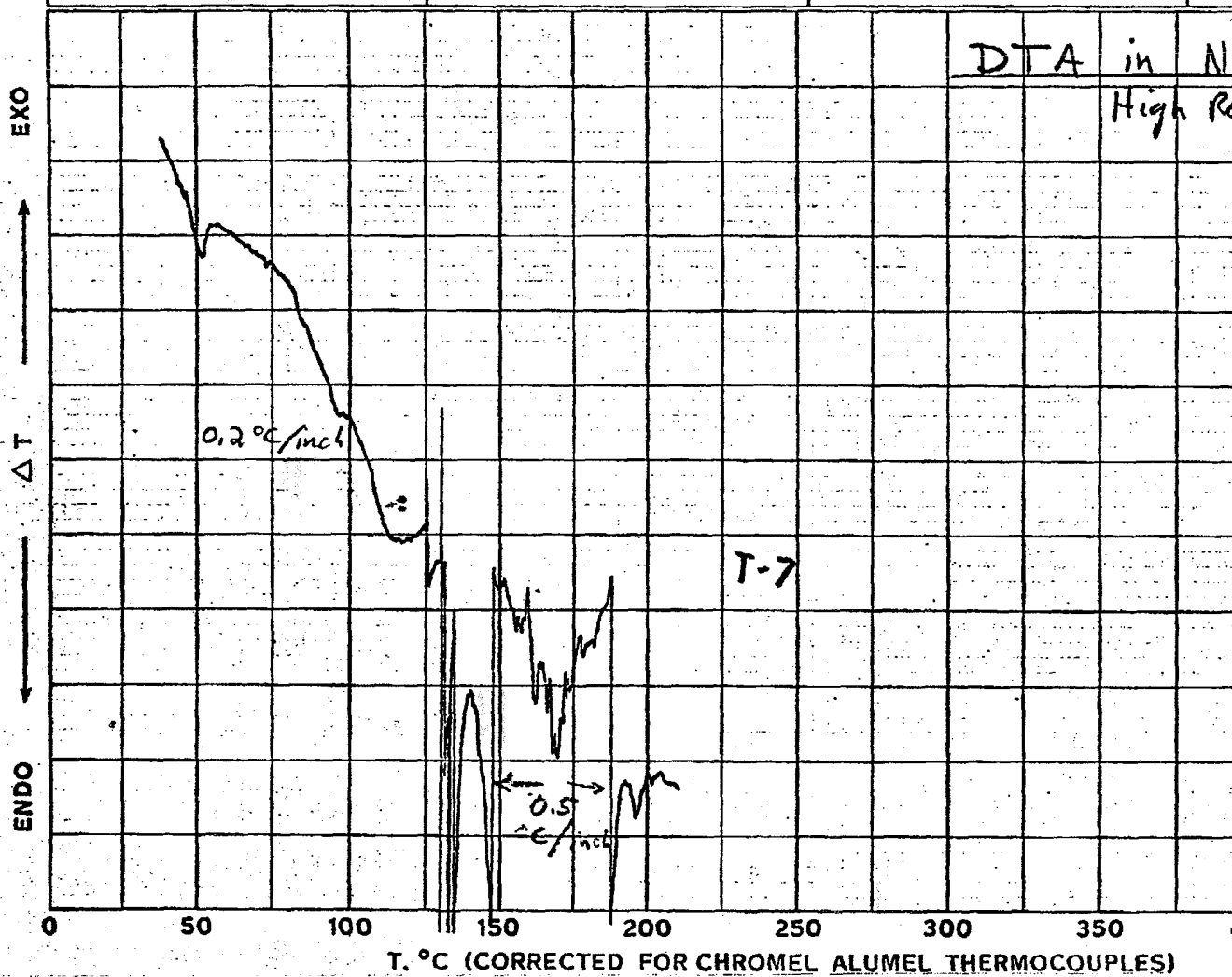
RATE 20 $\frac{^\circ\text{C}}{\text{min}}$ START $^\circ\text{C}$

ATM. O_2 -free N_2 , no flux

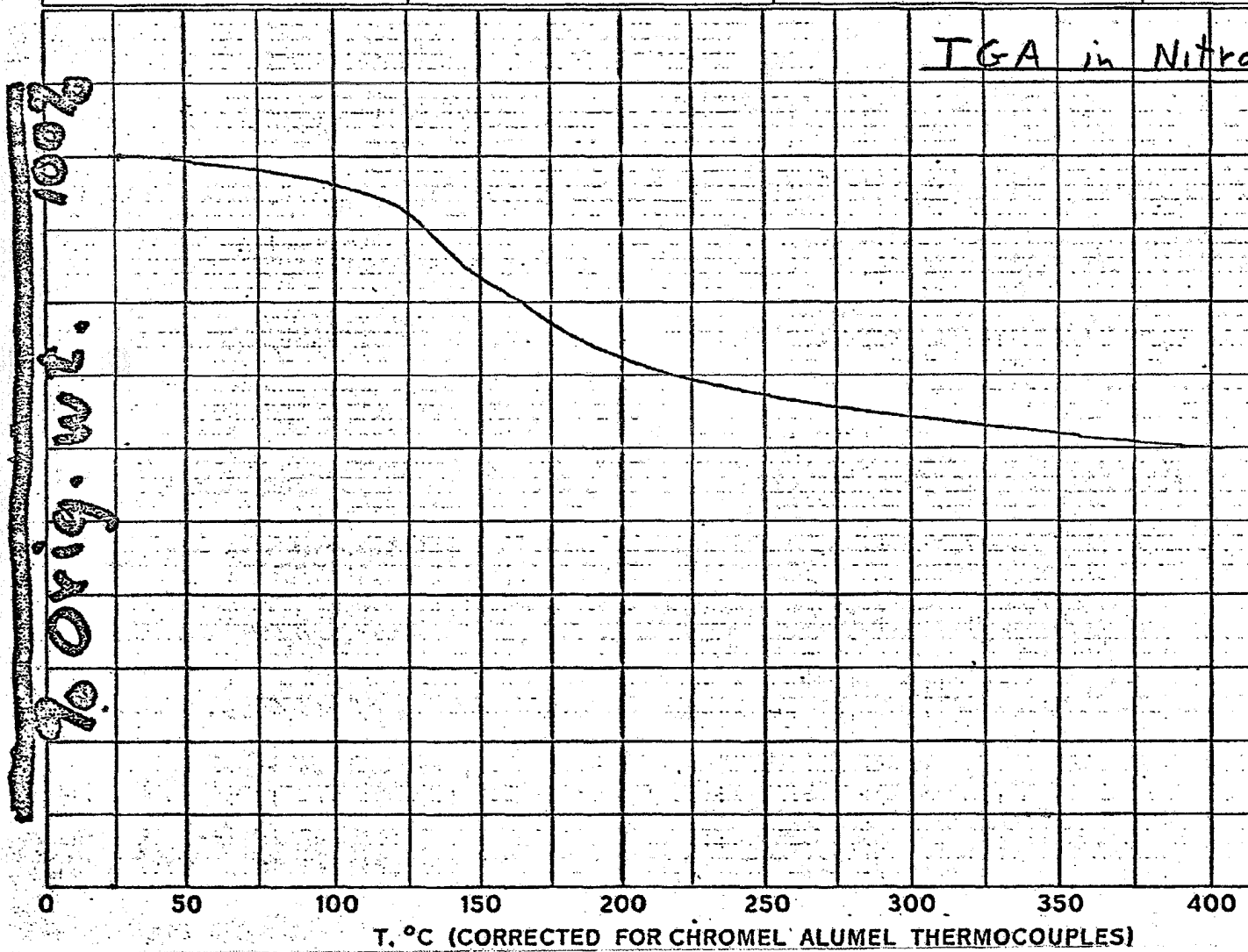
T ΔT

SCALE 50 $\frac{^\circ\text{C}}{\text{min}}$ 0.2 $\frac{^\circ\text{C}}{\text{min}}$

SETTING
Standard DTA



SAMPLE: T-7 CPC NaCl AlCl ₃	SIZE <u>6 mg</u>	ATM. <u>N₂</u>		RUN NO.
	REF. _____	T	ΔT	DATE <u>7</u>
ORIGIN:	PROGRAM MODE _____	SCALE SETTING <u>50</u> $\frac{mg}{\%}$		OPERAT
	RATE <u>20</u> $\frac{mg}{\%}$ START <u> </u> °C			



ACKNOWLEDGEMENT

The aid of Mrs. Margaret L. Greigg in the experimental program is gratefully acknowledged.

LITERATURE CITED

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