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Technical Report 92047

August 1992

Thermal Stability of Lithiated Vanadium Oxide (LVO), γ-Lithium Vanadium Bronze (γ-LiV_2O_5) and Vanadium Dioxide (VO_2) Thermal Battery Cathode Materials

by

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J. C. Bryce

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Farnborough

Technical Report 92047

Received for printing 29 July 1992

THERMAL STABILITY OF LITHIATED VANADIUM OXIDE (LVO), γ-LITHIUM VANADIUM BRONZE (γ-LiV_2O_5) AND VANADIUM DIOXIDE (VO_2) THERMAL BATTERY CATHODE MATERIALS

by

A. G. Ritchie
J. C. Bryce

SUMMARY

Thermal analysis of LVO has shown that it has limited thermal stability, possibly accounting for the failure of some thermal batteries with LVO cathodes. Its minor component, γ-LiV_2O_5, melts at temperatures which could be reached during thermal battery activation. The major component of LVO, VO_2, is thermally stable on its own, but can react with lithium chloride-potassium chloride binary eutectic when heated for prolonged periods above 700°C, though VO_2/binary eutectic mixtures should be sufficiently stable for use in thermal batteries.

Departmental Reference: Materials & Structures 357

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1 INTRODUCTION

One of the major research interests of the Battery Technology Section in the Materials and Structures Department in the Defence Research Agency (formerly the Royal Aircraft Establishment) at Farnborough has been the improvement of thermal batteries. These are high temperature reserve batteries, primarily used in missiles[1-5]. With the aim of obtaining higher energy density batteries, a new cathode material, lithiated vanadium oxide, has been developed[6-8] and successful batteries have been manufactured using this cathode material[9]. However, some further batteries have been less successful[10] and this may be due to inadequate thermal stability of the LVO, either on its own or mixed with thermal battery electrolytes[11]. The thermal stabilities of LVO itself, its major component, vanadium dioxide (VO_2), and its minor component, γ-lithium vanadium bronze (γ-LiV_2O_5) have been investigated both individually and mixed with molten salt electrolytes, as molten salts are commonly added to thermal battery cathode materials to improve cathode conductivity. The individual components of LVO have been investigated as these may be useful cathode materials[12].

2 EXPERIMENTAL

The thermal stabilities of LVO and its components have been investigated by thermal analysis using the techniques of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a PL Thermal Sciences (formerly Stanton Redcroft) STA 1000 thermal analyser. This instrument records weight changes (TGA) and temperature differences (DTA) simultaneously as a sample is heated at constant rate, enabling thermal effects and weight changes to be correlated. The traces plotted here are after baseline subtraction, in which blank runs with empty pans have been subtracted from the sample runs in order to eliminate, or at any rate reduce, baseline curvature. In some cases, slight residual baseline curvature is apparent, due to slight differences in baseline between sample and blank runs.

The LVO used was either 'B × 6' or 'Batch 2'. The latter material has actually been used in the manufacture of prototype thermal batteries. 'Washed' LVO was prepared by shaking LVO with water to dissolve out residual lithium bromide (and any other soluble impurities), pouring off the water, and drying the remaining LVO. The LiV_2O_5 was made by K. Warner[12] according to the method of Murphy *et al*[13]. The vanadium dioxide was bought from Aldrich and was in the low temperature stable monoclinic form[12].

The molten salt eutectics which were used were the common thermal battery electrolytes: binary eutectic (lithium chloride-potassium chloride, melting point 352°C) and ternary eutectic (lithium fluoride-lithium chloride-lithium bromide, melting point 445°C)[2].

The LVO samples were analysed for bromine content by A. Christopher (Analytical and General Chemistry Section).

3 RESULTS

3.1 Thermal analysis of LVO

Thermal analysis of LVO (B × 6)is shown in Fig 1. This shows weight loss in two steps with corresponding endotherms at around 50-120°C, presumably due to water loss, and an extra peak in the DTA due to the solid state transition in VO_2 at 68°C: 9.9% weight loss was found between around 450-750°C showing thermal instability of the LVO at temperatures which could be reached in thermal batteries. The endotherm at 529°C may be due to melting of residual lithium bromide in the LVO[8] (literature melting point, 552°C[2]). The broad endotherm at 600-700°C could be due either to the heat change for the process causing the 9.9% weight loss over roughly the same temperature range or it could be due to a solid state phase change in the LiV_2O_5 component of LVO (see below). The strong endotherm at 746°C is due to melting of the LiV_2O_5 (see below).

Batch 2 LVO showed generally similar behaviour to LVO B × 6 on thermal analysis. Water was lost at 20-120°C with 2 endotherms, one of which probably included the 68°C phase transition which would have overlapped the heat absorption due to evaporation of water: 4.1% weight loss occurred between around 400-570°C. The 746°C melting endotherm for LiV_2O_5 was not apparent in this case though a broad endotherm was found at around 670-750°C which could be due to either non-stoichiometric $Li_xV_2O_5$ or to a mixture of vanadium bronzes.

Both samples showed weight losses starting at about 450°C. These weight losses can be correlated with the bromine content of the samples. LVO B × 6 lost 9.9% from an initial 13.4% bromine content and Batch 2 lost 4.1% from a initial 6.1% bromine content[11]. This suggests that heating the LVO completed the reaction from which the LVO was made (vanadium oxide V_6O_{13} + lithium bromide LiBr forming LVO[8,9]) and that the bromine was evolved during heating. Bromine is an exceedingly reactive and corrosive material, particularly at high temperatures, and bromine evolution could severely damage thermal batteries, possibly accounting poor performance of some batteries using LVO cathodes[10].

3.2 Thermal analysis of LiV_2O_5

Thermal analysis of LiV_2O_5 (the minor component of LVO) is shown in Fig 3. Weight is lost up to around 150°C, presumably due to loss of absorbed water, and then the weight is stable. The first endotherm in the DTA trace at 590°C is presumably due to a solid state phase change and the second endotherm (at 753°C) is due to the melting of LiV_2O_5 (literature value for melting point 772°C[14]). A phase change at 590°C (a temperature which could readily be reached in thermal battery operation) could cause dimensional instability in a cathode pellet and hence problems could arise in thermal battery operation. The melting point of LiV_2O_5 (753°C) is well above normal thermal battery operating temperatures but it is a temperature which would almost certainly be surpassed at the surface of the cathode pellet in contact with the heat pellet as iron-potassium perchlorate heat pellets can reach temperatures over 1000°C as they burn during the activation of the battery. Melting of the LiV_2O_5 component of the cathode during battery activation is therefore possible and migration of molten LiV_2O_5 could cause internal short circuits during battery activation and consequent poor performance.

3.3 Thermal analysis of vanadium dioxide

Thermal analysis of vanadium dioxide (Fig 4) showed an endotherm due to the solid state phase change from monoclinic to tetragonal forms at 68°C. The observed temperature (63°C) is slightly low due to difficulty in temperature calibration at the low end of the temperature range. A small endotherm is observed at 687°C, close to the melting point of vanadium pentoxide, V_2O_5, at 674°C. It is possible that hot VO_2 had gettered slight traces of oxygen in the argon gas flow and had been slightly oxidised on the surface. A repeat run on the same sample (Fig 5) showed a very similar thermal analysis trace but the high temperature peak had split into two and these were slightly more pronounced than in the first run. The weight increased slightly during both runs, possibly due to slight oxidation or to balance drift. As there was no significant weight change during both runs and as there was no significant change between the two runs, it has been shown that, as expected, vanadium dioxide is physically and chemically stable on heating in inert atmosphere to at least the maximum temperature of the first run (764°C), in contrast to LVO and LiV_2O_5, which suffered weight loss and melting, respectively.

3.4 Thermal analysis of binary and ternary eutectics

In order to determine the thermal stability of LVO, LiV_2O_5 and VO_2 mixtures with binary or ternary eutectics, it is necessary first to determine the thermal stabilities of these molten salt mixtures on their own. Five successive thermal analysis runs were done on a sample of binary eutectic (see Figs 6 to 10). The first run (Fig 6) showed weight loss at around 100°C with the corresponding water evaporation endotherm. The weight then remained constant up to the maximum temperature of this run (555°C). A repeat run (up to 655°C) also showed a steady weight. Further runs (up to 758, 860 and 959°C) showed increasing weight loss as the temperature was increased with weight losses starting at 650-700°C and progressively more weight being lost as the temperature was increased up to the maximum for each run. These high temperature weight losses are almost certainly due to evaporation of the molten salts from the open platinum pans into the argon gas stream. All runs showed strong melting endotherms with onset temperatures in the range 355-358°C, close to the literature value for the melting point of binary eutectic (352°C)[2]. The melting endotherms were all sharp, indicating that the mixtures were eutectic and that no composition changes were taking place during heating. The evaporation of the binary eutectic above around 700°C is important as some salt eutectic is normally added to thermal battery cathodes to improve ionic conductivity and cathodes could be heated above the salt evaporation temperatures during thermal battery activation.

Ternary eutectic showed very similar thermal properties to binary eutectic (see Figs 11 to 15). Water was lost on the first run (Fig 11) at about 100°C, then weights were constant up to 500-600°C, above which weight is progressively lost at higher temperatures, presumably due to evaporation of the molten salt. The melting endotherms were always sharp, showing that the salt mixture remained eutectic. The temperatures for onset of melting were 442-445°C, close to the literature values of 445°C[2].

3.5 Thermal analysis of LVO/binary mixtures

Thermal analysis of LVO/binary mixtures was done to check for interactions between the cathode material (LVO) and the molten salt electrolyte (binary eutectic). Results for 'washed' LVO/binary mixtures are shown in Figs 16 to 19. Thermal analysis of 'washed' LVO/binary mixtures (Fig 16) showed water loss at 50-100°C but then a steady weight trace up to around 650°C, *ie* the weight loss seen for untreated LVO at 400-500°C was absent. One of the low temperature (~60°C) endotherms is probably the 68°C phase transition in VO_2 and a strong melting endotherm at 350°C was seen for binary eutectic melting. The broad peak centred around 600°C for LiV_2O_5 was also present. The repeat run (Fig 17) showed a small phase transition for VO_2 with no weight change, at 53°C, rather below the 68°C phase transition for VO_2, a strong melting endotherm for binary electrolyte at 345°C and the LiV_2O_5 transition centred around 612°C. The comparatively small changes between these two runs indicates that the 'washed' LVO is stable to heating with binary eutectic up to the maximum temperature of the first run (665°C). The second repeat (Fig 18) showed water loss following water absorption during overnight storage in the thermal analyser, then a smaller binary melting peak at 342°C with an extra peak around 530°C. This indicates that heating to 761°C in the first repeat had caused some reaction within the LVO/binary mixture. The third repeat (Fig 19) (after heating to 859°C in the second repeat) showed only a very small VO_2 transition (nominally at 68°C), the binary melting peak (now reduced to 332°C) was small and a very large extra peak was found centred at 442°C. Clearly large changes to the mixture had occurred. Substantial weight loss occurred above around 700°C, presumably due to evaporation of the binary eutectic.

3.6 Thermal analysis of VO_2/binary mixtures

The first run (Fig 20) shows weight loss at 50-100°C from water evaporation from the hygroscopic salt overlapping the 68°C phase transition of VO_2 and a strong endotherm for melting of the binary electrolyte at 354°C. Run 2 (Fig 21) shows again the VO_2 phase transition and the binary melting (at 352°C) with a small peak starting at 574°C. This shows that the binary/VO_2 mixture reacts very little up to the temperature limit of the first run (551°C). The third run (Fig 22) showed a fairly strong VO_2 phase transition and a strong melting endotherm for binary melting with a slightly increased peak around 600°C. The fourth run (Fig 23) showed a much reduced VO_2 phase transition and an increased peak around 600°C but still a strong binary melting endotherm. These results show increasing reaction as the sample was heated to progressively higher temperatures but significant reaction had occurred only after the third run (heating to 758°C) so VO_2/binary eutectic mixtures are reasonably stable at normal thermal battery operating temperatures (up to around 600°C). Weight loss due to evaporation of binary eutectic occurred above about 600°C.

3.7 Thermal analysis of VO_2/ternary mixtures

Thermal analyses of 70% VO_2:30% wt ternary eutectic mixtures are shown in Figs 24 to 27. The results are similar to VO_2:binary eutectic mixtures. The first run (Fig 24) shows weight loss due to water evaporation from the very hygroscopic ternary salt with the corresponding endotherm for the heat absorption peaking at around 130°C. Subsequent repeat runs showed little water loss, indicating that the sample had remained dry during storage in the thermal analyser in a dry argon gas flow. The VO_2 phase transition (observed at around 60°C) decreased in intensity with repeated runs and was only just detectable in the fourth run (Fig 27), after heating to 758°C in the third run. The ternary eutectic melting was observed with onset temperatures of 437-444°C (*cf* literature value 445°C[2]). The area of the ternary melting endotherm was noticeably reduced by the fourth run, as some ternary salt had evaporated on heating to temperatures above around 600°C. Extra peaks were observed on the high temperature side of the ternary salt melting endotherm, indicating some change in composition of the eutectic, either due to reaction with the VO_2 or to differential evaporation rates of the three components of the ternary eutectic.

3.8 Thermal analysis of VO_2/LiCl, LiBr mixtures

In order to study the reaction of vanadium dioxide with binary and ternary eutectics more closely, the thermal analyses of vanadium dioxide with the lithium chloride and bromide components of these mixtures have also been recorded. The first run with lithium bromide (Fig 28) showed the normal VO_2 phase transition (observed at 63°C) and the water loss from the very hygroscopic lithium bromide. The onset of melting for lithium bromide was 533°C (rather below the literature value of 552°C[2]) and weight was lost (presumably lithium bromide evaporation) above about this temperature. The repeat run (Fig 29), after heating to 760°C in the first run, showed a constant weight and no lithium bromide melting, indicating that all the lithium bromide had been lost during the first run. The VO_2 phase transition had also disappeared but a new peak had been found at 700°C, showing some change to the VO_2. VO_2 is clearly not stable to heating to 760°C with lithium bromide.

The thermal analysis of lithium chloride with VO_2 was observed up to 657°C (about 100°C lower than used for lithium bromide). The first run (Fig 30) showed weight loss due to water evaporation from the hygroscopic salt at around 100°C, the phase transition of VO_2, observed at 63°C, melting of the lithium chloride at 587°C (literature value 610°C[2]) and slight weight loss above around 500°C (lithium chloride evaporation). The repeat run (Fig 31), after heating in the first run to 657°C, showed the VO_2 phase transition, lithium chloride melting (at 568°C) with a slight additional peak to the high temperature side of the main peak. Hence only slight reaction had occurred on heating VO_2 with lithium chloride to 657°C.

4 DISCUSSION

The purpose of this work was to examine the thermal stability of lithiated vanadium oxide (LVO) and its principal components, vanadium dioxide (VO_2) and γ-lithium vanadium bronze (γ-LiV_2O_5), both on their own and mixed with the common thermal battery salts, binary and ternary eutectics, to determine if any thermal instabilities or interactions could account for the poor performance of some thermal batteries using LVO and to investigate if these problems also occurred for VO_2 and γ-LiV_2O_5 separately. Thermal analysis of LVO has shown that it is not thermally stable; it loses weight on heating and the weight loss roughly corresponds to the bromine content, suggesting that bromine is evolved on heating. VO_2 is thermally stable on heating, as expected. LiV_2O_5 is thermally stable but melts at around 750°C which is rather low for thermal battery use as temperatures well in excess of this could be reached during thermal battery activation. The binary and ternary eutectic salts, which are added to thermal battery cathodes to improve the ionic conductivity, are chemically stable but evaporate increasingly as the temperature is increased. 'Washed' LVO/binary mixtures from which the residual lithium bromide in the LVO had been removed surprisingly did not show the weight loss observed for LVO on its own, nor was the melting peak for the LiV_2O_5 component observed. Some reaction may have occurred on treating the LVO with water to dissolve out lithium bromide. Vanadium dioxide has been reported to be stable to binary eutectic at 450°C[15] and this has been confirmed in the present work. However reaction does occur on heating to progressively higher temperatures and little VO_2 remains after heating VO_2/binary mixtures to 750°C. VO_2/ternary eutectic mixtures also react at this temperature, though the nature of the product is unknown.

The better thermal stability of VO_2 compared with LVO (or LiV_2O_5) suggests it may be a preferable thermal battery cathode material to LVO, particularly as it is readily available as a pure chemical compound and as its electrochemical performance is at least as good as LVO, except possibly at the highest current densities[12].

5 CONCLUSIONS

Lithiated vanadium oxide (LVO) has limited thermal stability. It loses weight on heating (probably due to bromine evolution) and its minor component γ-lithium vanadium bronze (γ-LiV_2O_5) melts at temperatures which could be reached during thermal battery activation. These factors could account for the problems which have occurred in some thermal batteries using LVO cathodes. The major component of LVO, vanadium dioxide (VO_2), is stable to heating on its own and is also stable to heating with binary eutectic up to around 700°C but prolonged heating above this temperature causes reaction. Hence VO_2 may be a better thermal battery cathode material than LVO, as previous work has shown that its electrochemical performance is very similar to that of LVO in laboratory tests.

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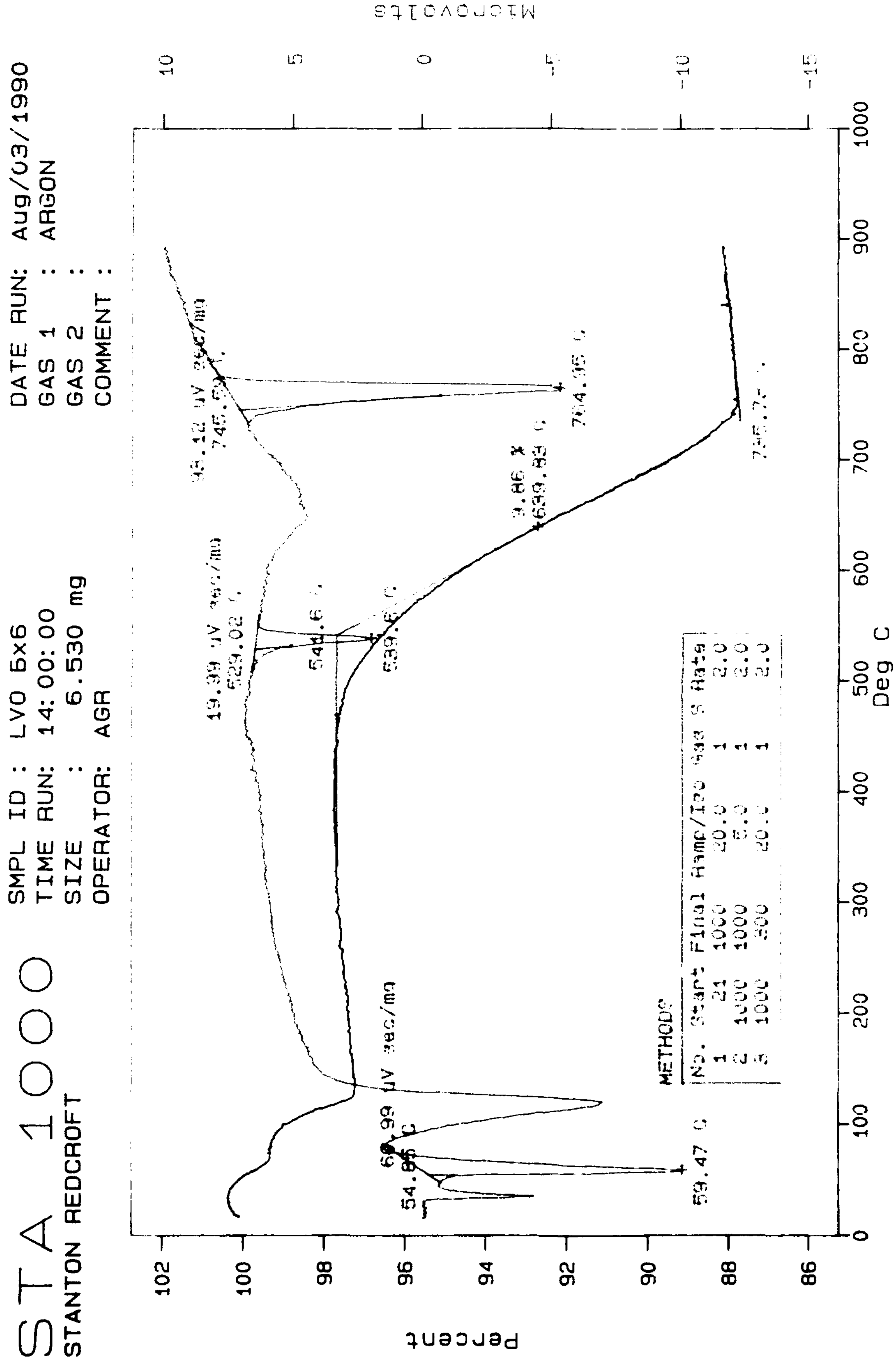
Fig 1


STA 1000

STANTON REDCROFT

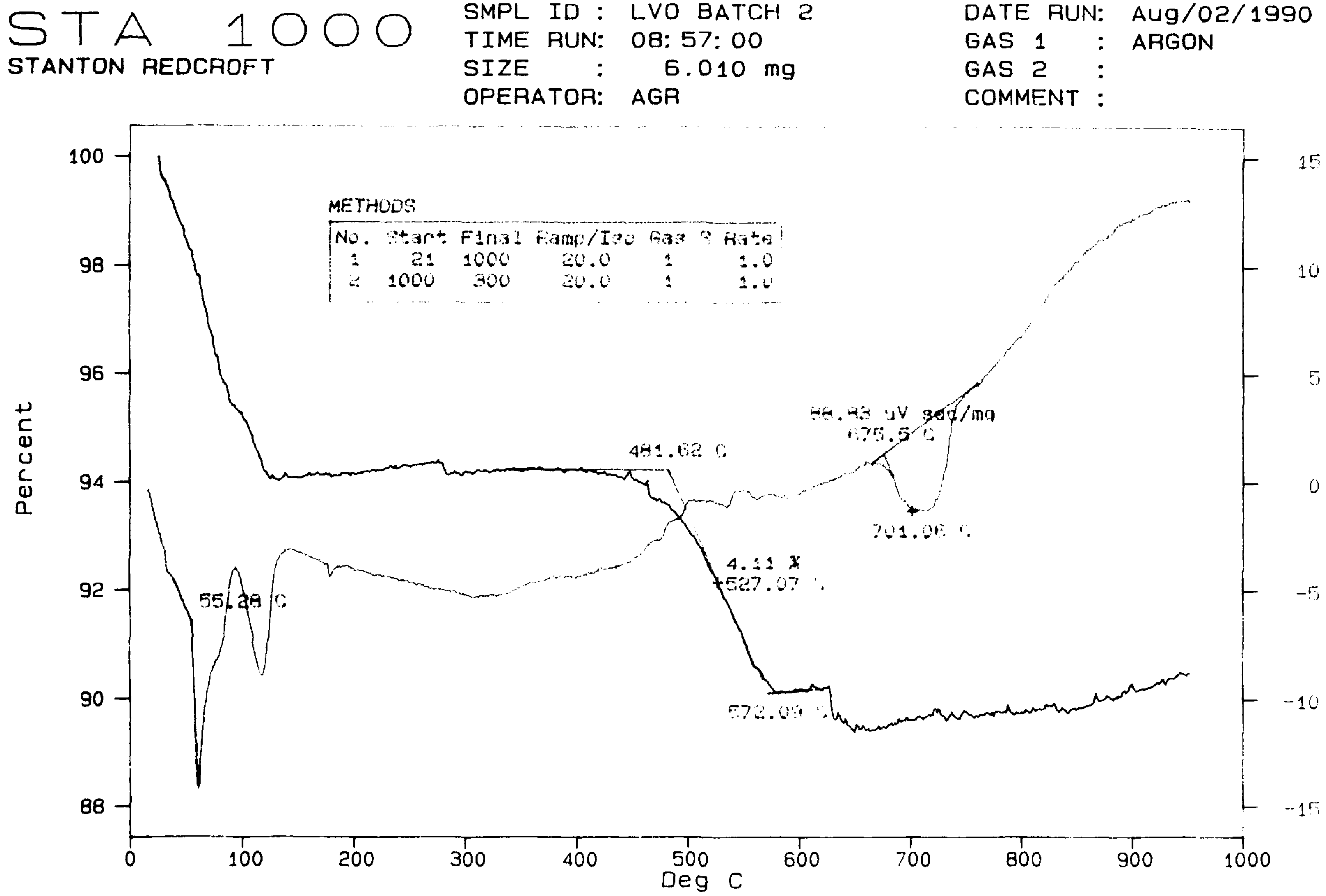
SMPL ID : LVO Bx6
TIME RUN: 14:00:00
SIZE : 6.530 mg
OPERATOR: AGR

DATE RUN: Aug/03/1990
GAS 1 : ARGON
GAS 2 :
COMMENT :

METHODS

No.	Start	Final	Ramp/Iso	Gas	S Rate
1	21	1000	20.0	1	2.0
2	1000	1000	5.0	1	2.0
3	1000	200	20.0	1	2.0

Fig 1 Thermal analysis of LVO B x 6



STA 1000
STANTON REDCROFT

SMPL ID : LVO BATCH 2
TIME RUN: 08:57:00
SIZE : 6.010 mg
OPERATOR: AGR

DATE RUN: Aug/02/1990
GAS 1 : ARGON
GAS 2 :
COMMENT :

METHODS

No.	Start	Final	Ramp/Iso	Gas ?	Rate
1	21	1000	20.0	1	1.0
2	1000	300	20.0	1	1.0

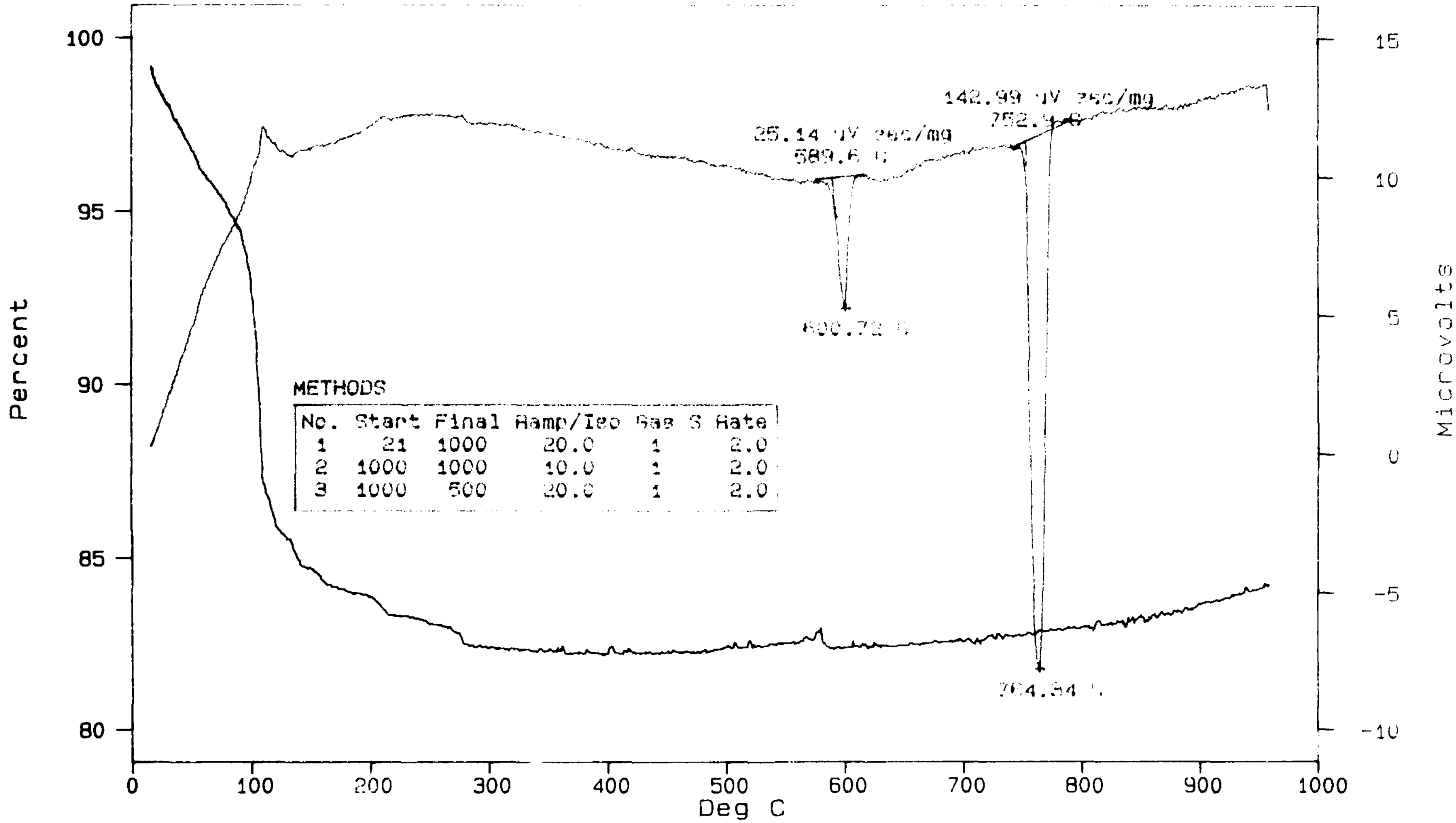
Fig 2 Thermal analysis of LVO Batch 2

Fig 3

STA 1000
STANTON REDCROFT

SMPL ID : LiV205
TIME RUN: 14:27:00
SIZE : 5.289 mg
OPERATOR: AGR

DATE RUN: Aug/02/1990
GAS 1 : ARGON
GAS 2 : Made by
COMMENT : K.Warner



METHODS

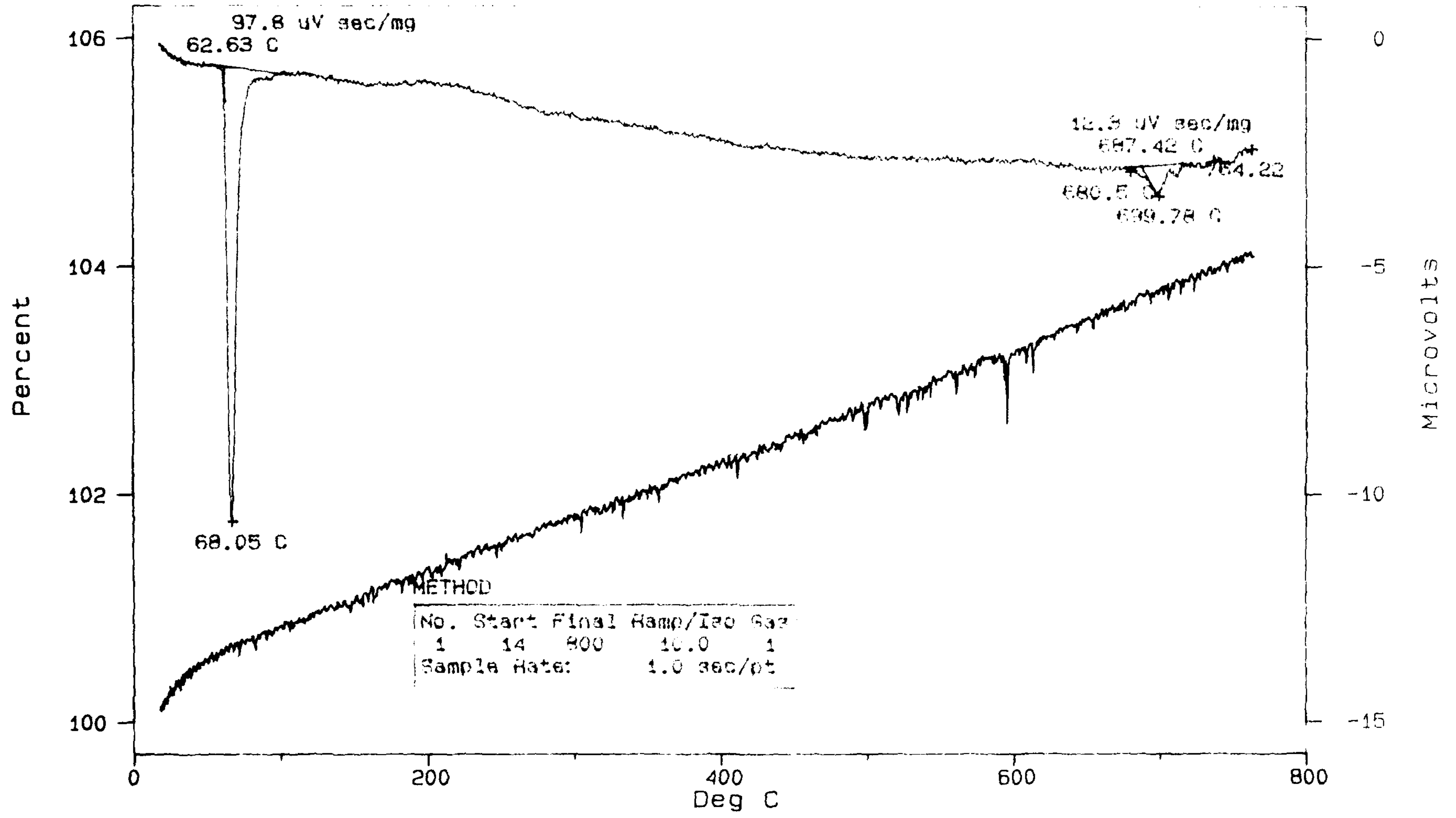
No.	Start	Final	Ramp/Iso	Gas	S Rate
1	21	1000	20.0	1	2.0
2	1000	1000	10.0	1	2.0
3	1000	500	20.0	1	2.0

Fig 3 Thermal analysis of α – lithium vanadium bronze

STA 1000
STANTON REDCROFT

SMPL ID : V02(Aldrich)
RUN ID :
SIZE : 5.348 mg
OPERATOR: JB

DATE RUN: Nov/28/1991
GAS 1 : Argon
COMMENT1: Pt pans
COMMENT2: Purged 45 min.



METHOD

No.	Start	Final	Ramp/Iso	Gas
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Sample Rate: 1.0 sec/pt

Fig 4 Thermal analysis of vanadium dioxide Run 1

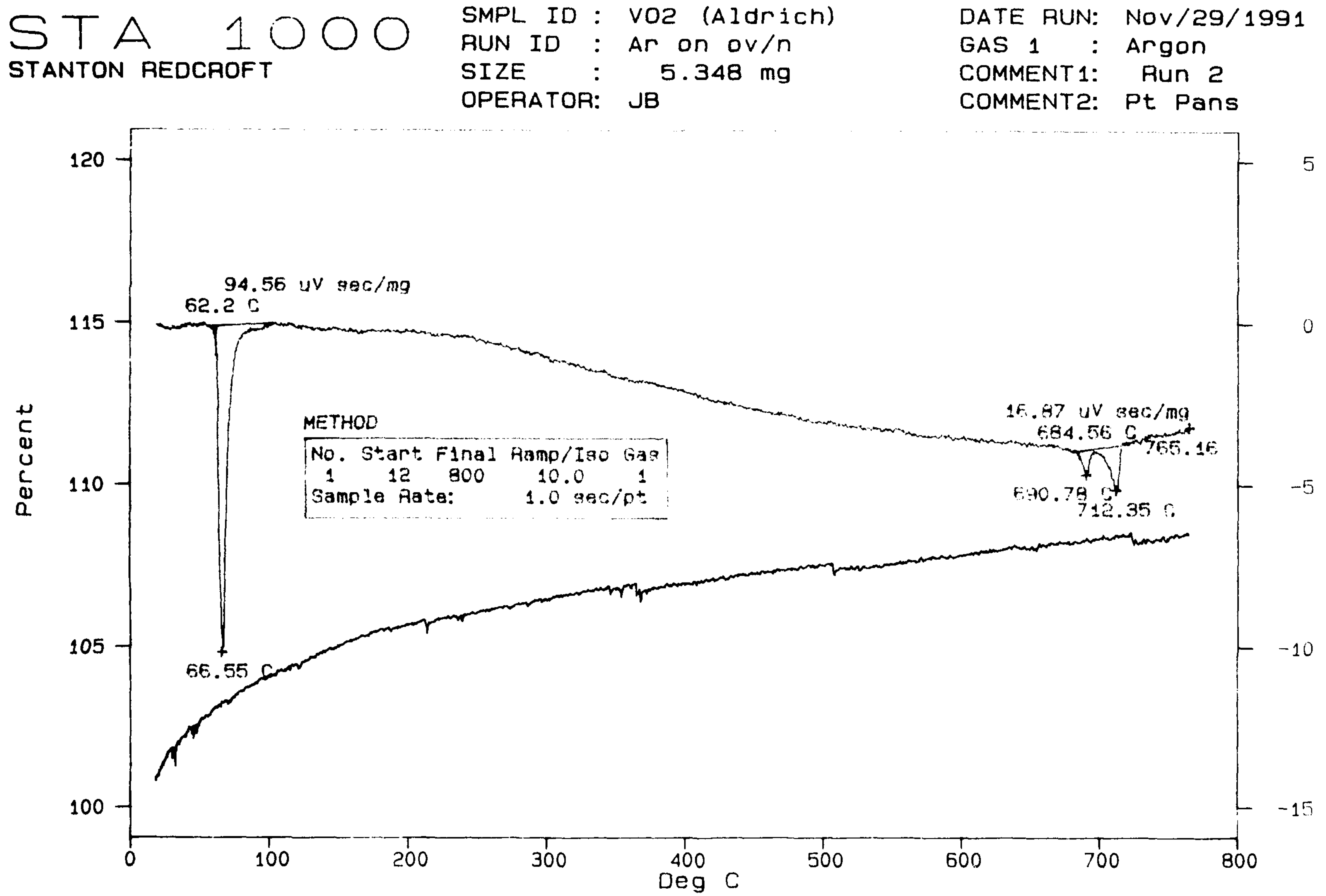
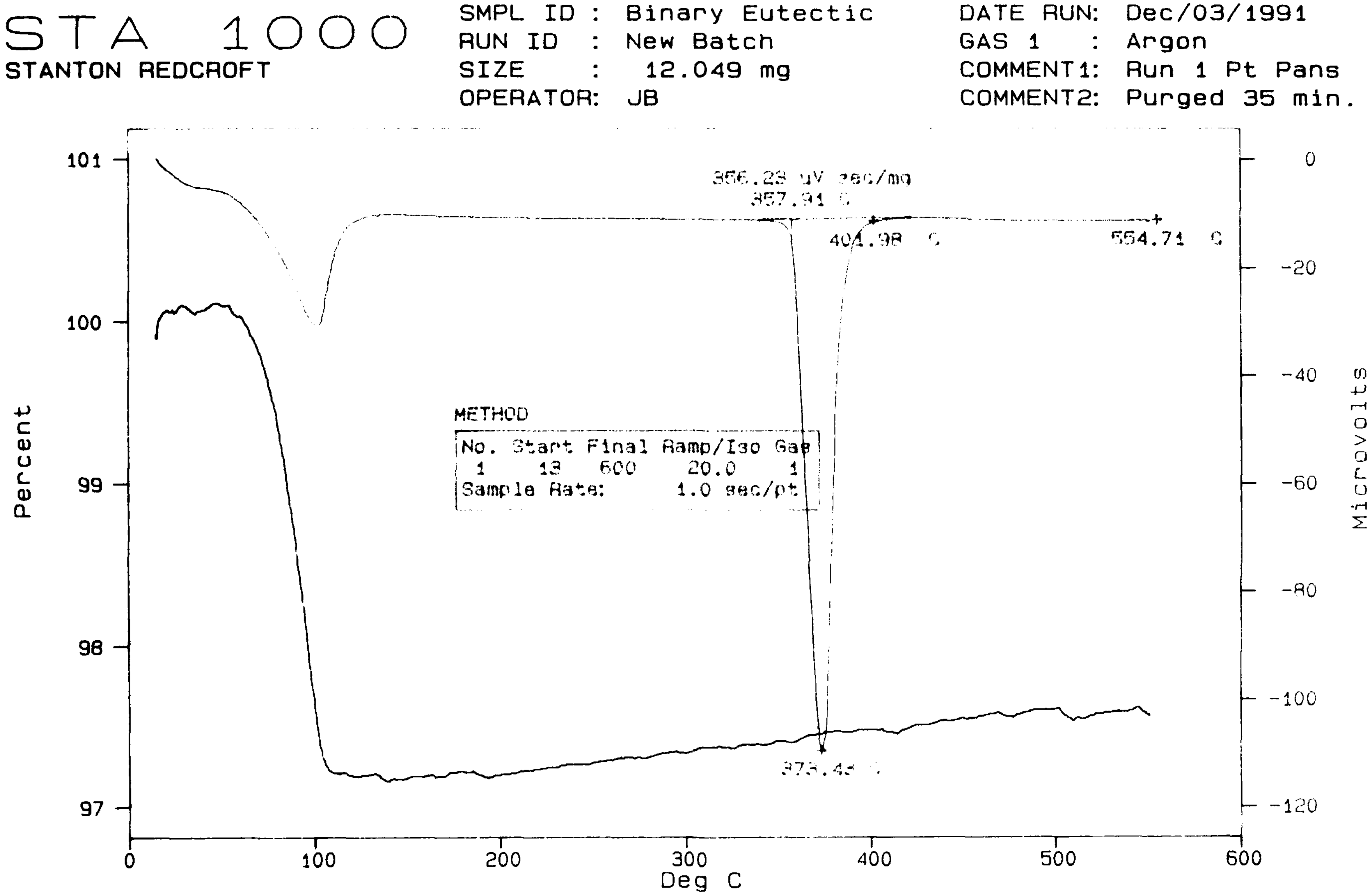


Fig 5 Thermal analysis of vanadium dioxide Run 2

Fig 5



STA 1000
STANTON REDCROFT

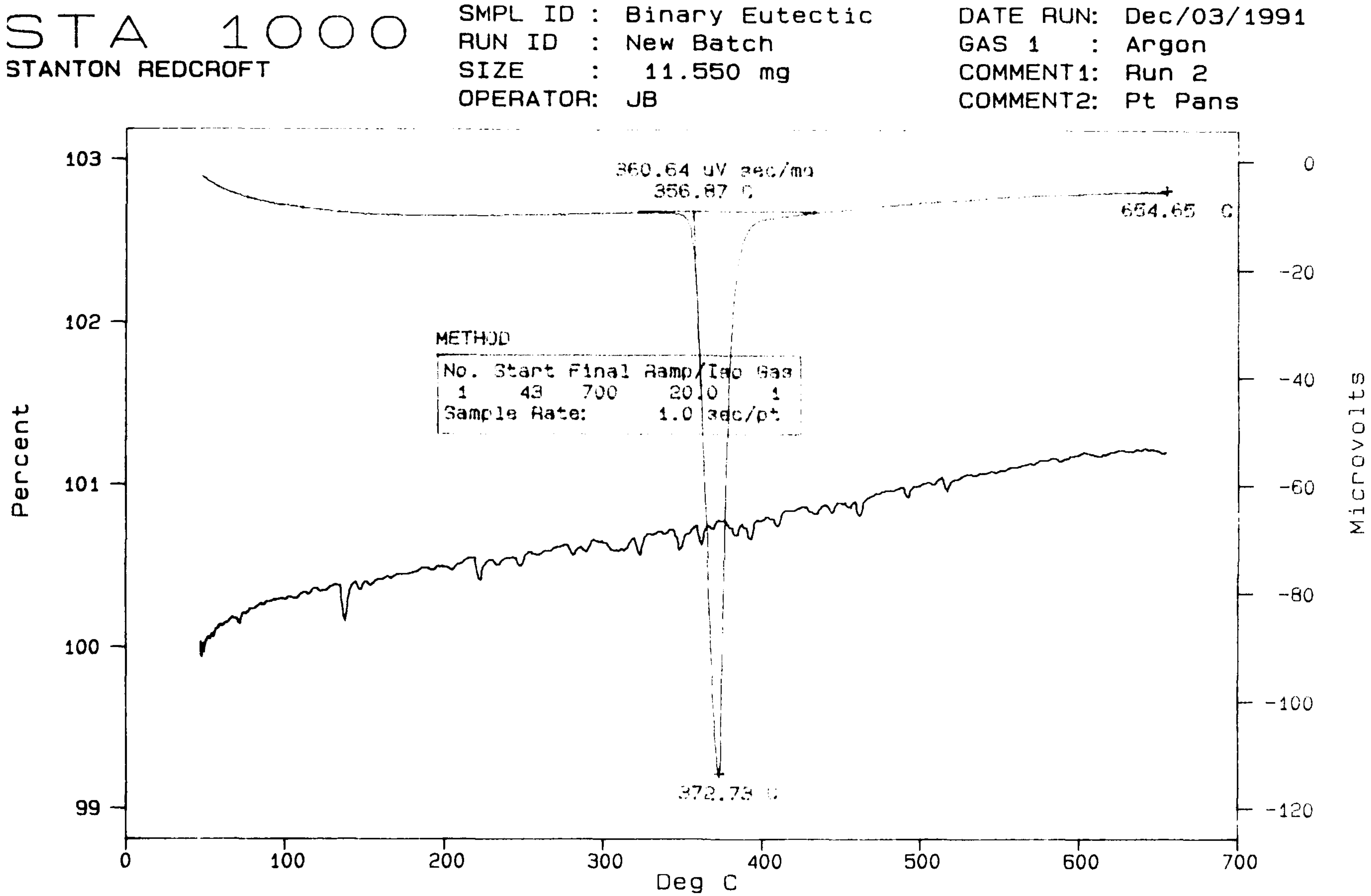
SMPL ID : Binary Eutectic
RUN ID : New Batch
SIZE : 12.049 mg
OPERATOR: JB

DATE RUN: Dec/03/1991
GAS 1 : Argon
COMMENT1: Run 1 Pt Pans
COMMENT2: Purged 35 min.

METHOD

```
No. Start Final Ramp/Iso Gas
 1    13   600    20.0    1
Sample Rate:      1.0 sec/pt
```

Fig 6 Thermal analysis of lithium chloride - potassium chloride eutectic Run 1



STA 1000
STANTON REDCROFT

SMPL ID : Binary Eutectic
RUN ID : New Batch
SIZE : 11.550 mg
OPERATOR: JB

DATE RUN: Dec/03/1991
GAS 1 : Argon
COMMENT1: Run 2
COMMENT2: Pt Pans

METHOD

No.	Start	Final	Ramp/Iso	Gas
1	43	700	20.0	1

Sample Rate: 1.0 sec/pt

Fig 7 Thermal analysis of lithium chloride - potassium chloride eutectic Run 2

Fig 8

STA 1000
STANTON REDCROFT

SMPL ID : Binary Eutectic
RUN ID : New Batch
SIZE : 11.530 mg
OPERATOR: JB

DATE RUN: Dec/03/1991
GAS 1 : Argon
COMMENT1: Run 3
COMMENT2: Pt Pans

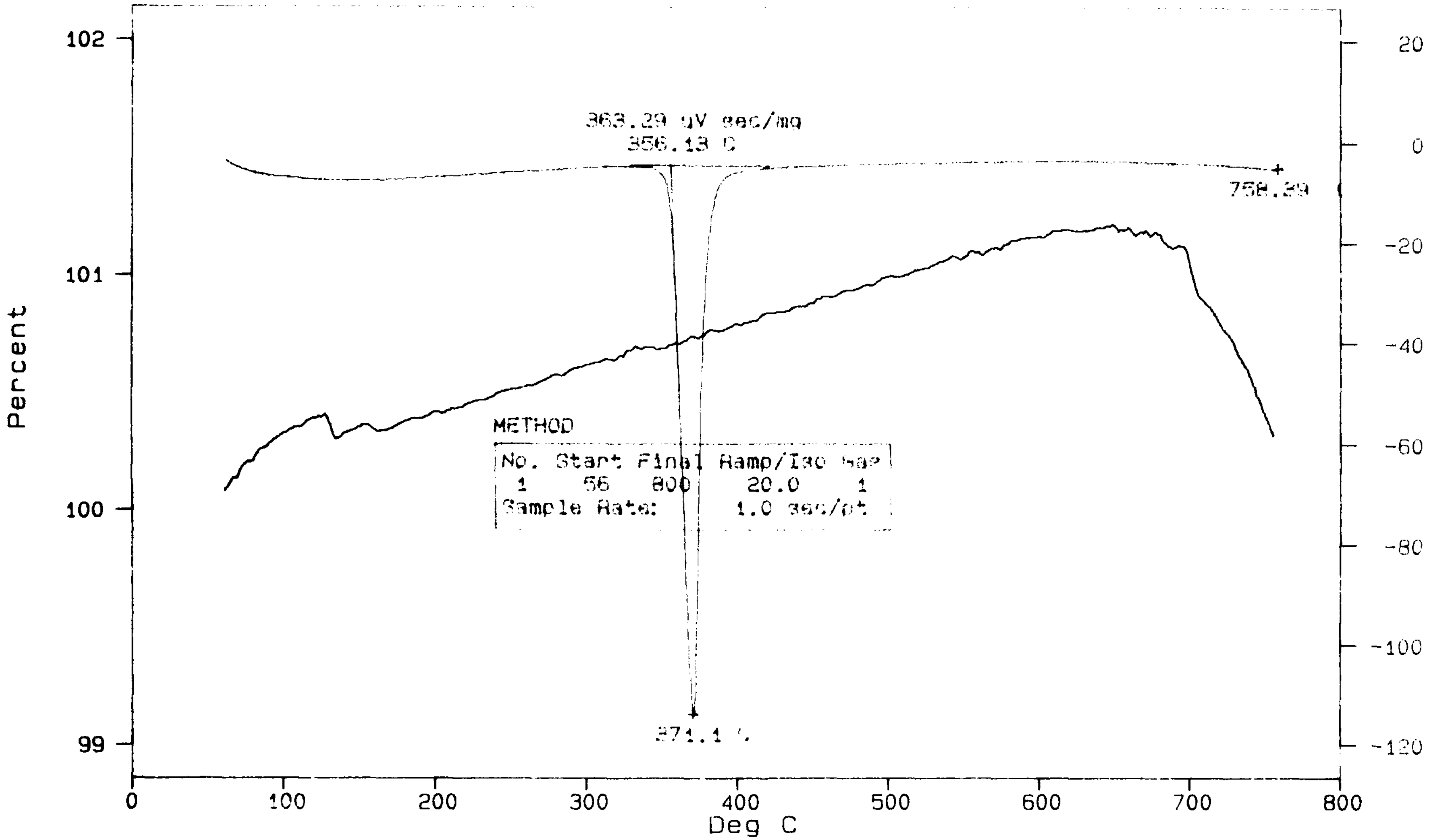


Fig 8 Thermal analysis of lithium chloride - potassium chloride eutectic Run 3

Fig 9

STA 1000
STANTON REDCROFT

SMPL ID : Binary Eutectic
RUN ID : New Batch
SIZE : 11.170 mg
OPERATOR: JB

DATE RUN: Dec/03/1991
GAS 1 : Argon
COMMENT1: Run 4
COMMENT2: Pt Pans

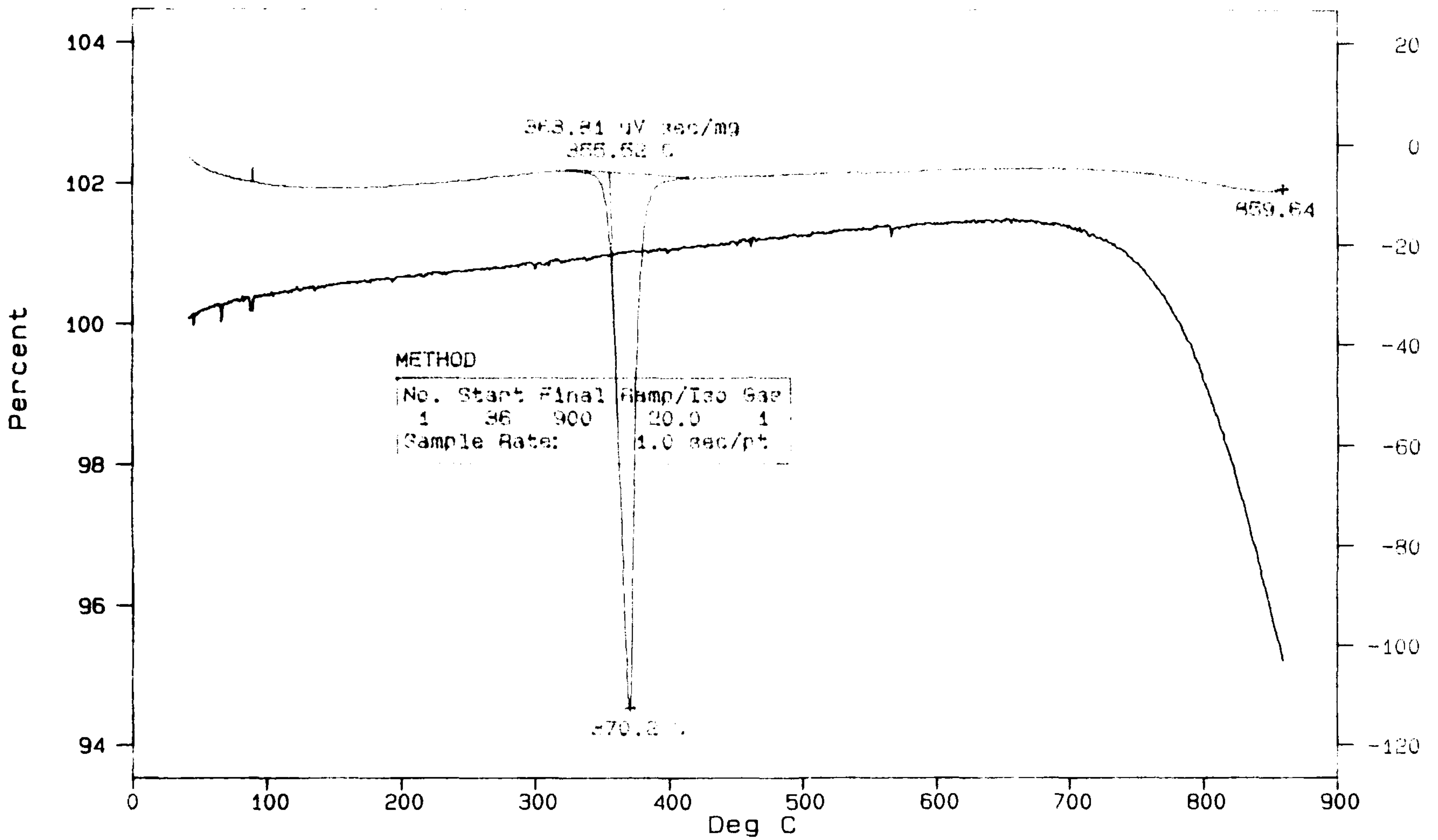
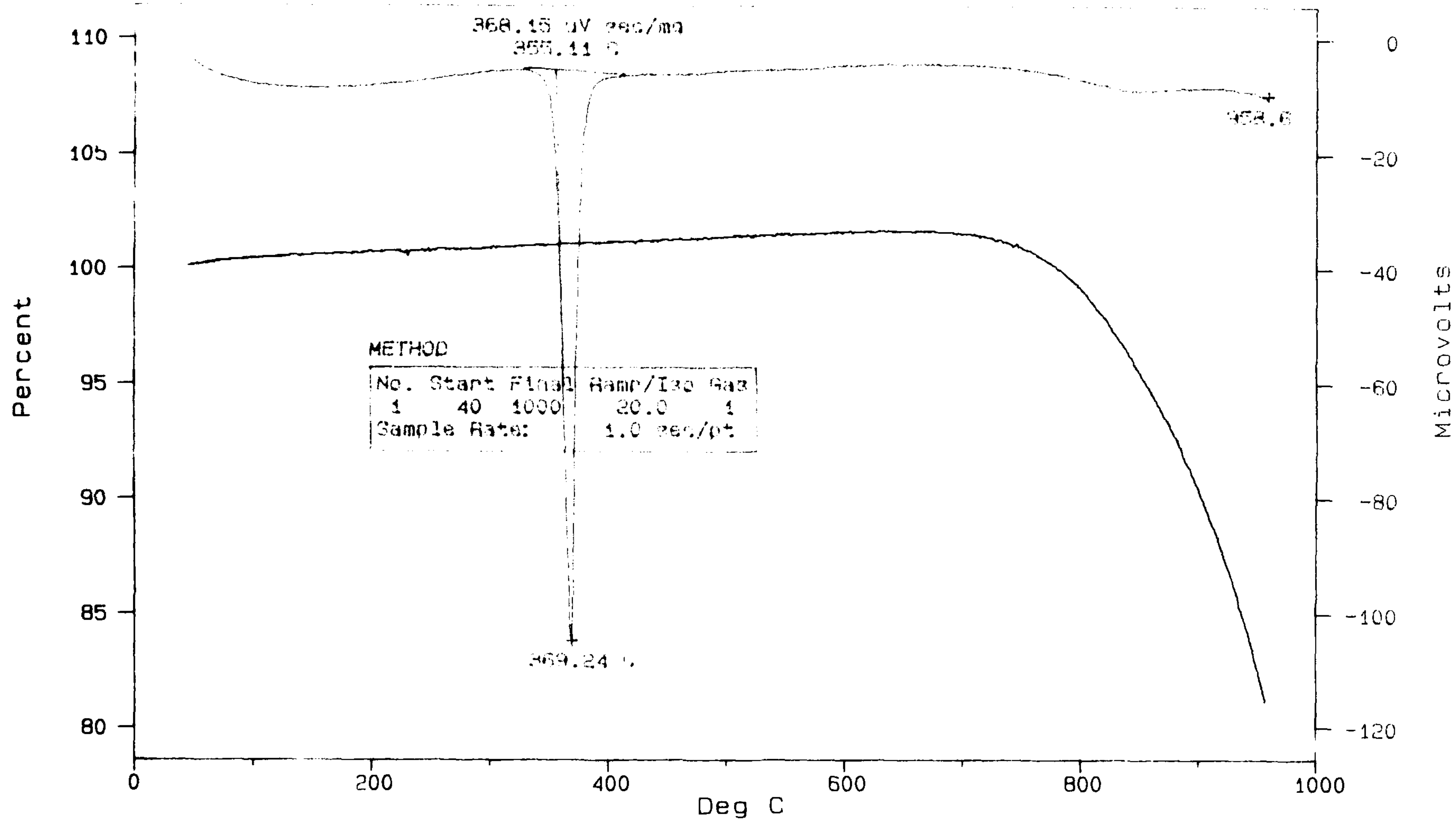


Fig 9 Thermal analysis of lithium chloride - potassium chloride eutectic Run 4

STA 1000
STANTON REDCROFT

SMPL ID : Binary Eutectic
RUN ID : New Batch
SIZE : 9.990 mg
OPERATOR: JB

DATE RUN: Dec/03/1991
GAS 1 : Argon
COMMENT1: Run 5
COMMENT2: Pt Pans



METHOD

No.	Start	Final	Ramp/Iso	Gas
1	40	1000	20.0	1
Sample Rate:			1.0 sec/pt	

Fig 10 Thermal analysis of lithium chloride - potassium chloride eutectic Run 5

STA 1000
STANTON REDCROFT

SMPL ID : Ternary Eutectc
RUN ID : New Batch
SIZE : 12.683 mg
OPERATOR: JB

DATE RUN: Dec/05/1991
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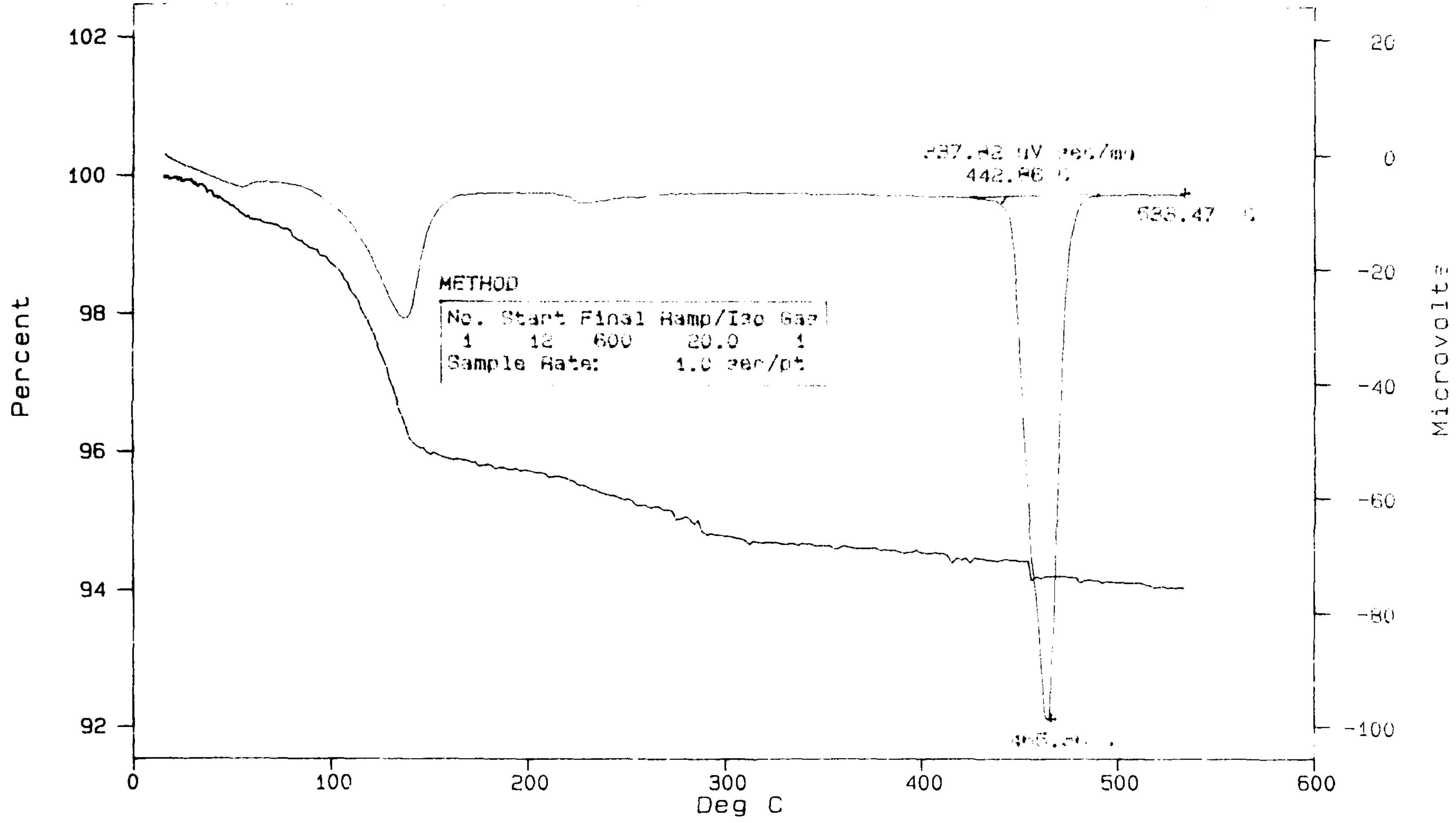
COMMENT1: Run 1 Pt Pans
COMMENT2: Purged 30 min.

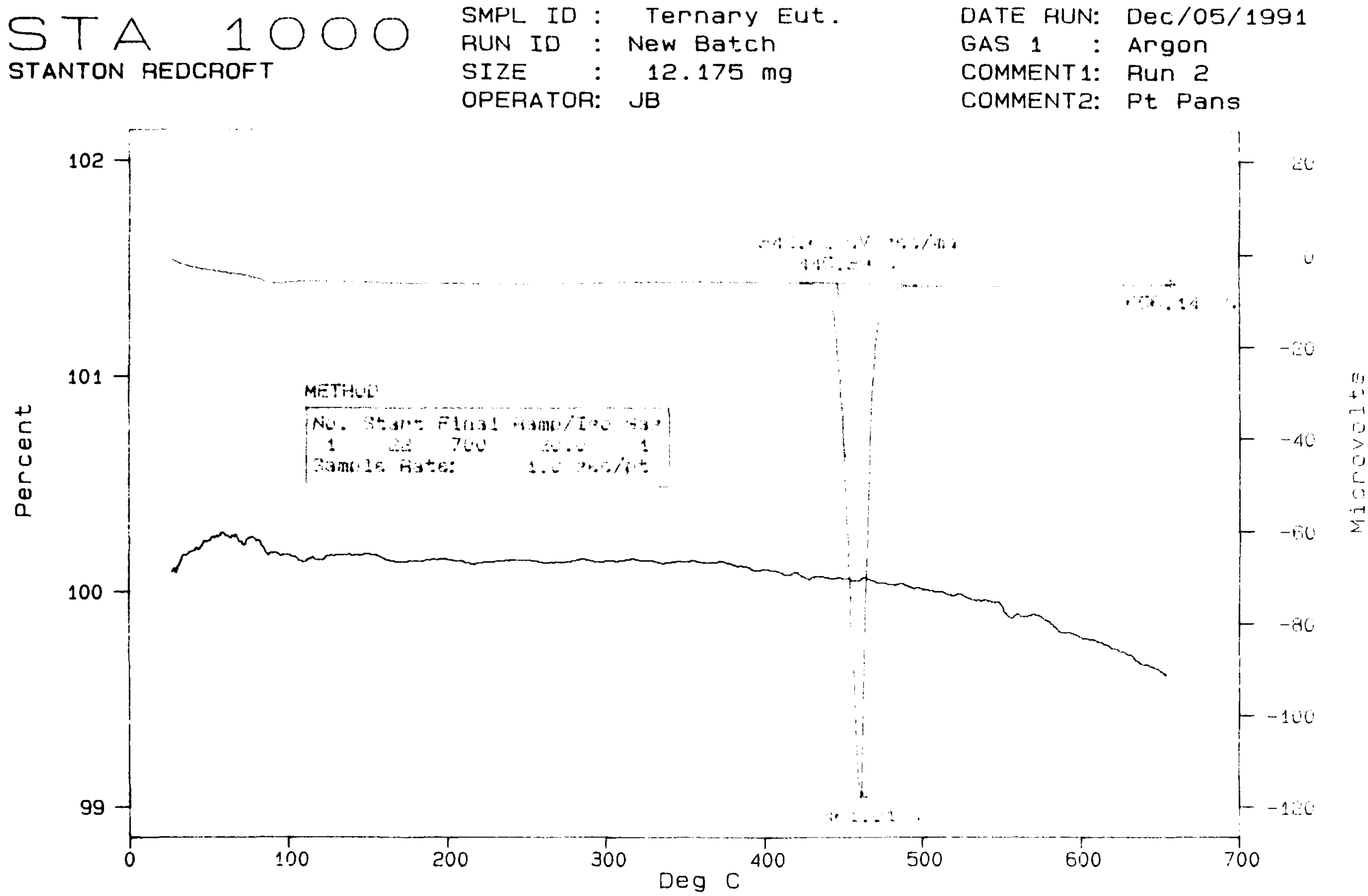


METHOD

No.	Start	Final	Ramp/Iso	Gas
1	12	600	20.0	1

Sample Rate: 1.0 sec/pt

Fig 11 Thermal analysis of lithium fluoride - lithium chloride - lithium bromide eutectic Run 1



STA 1000
STANTON REDCROFT

SMPL ID : Ternary Eut.
RUN ID : New Batch
SIZE : 12.175 mg
OPERATOR: JB

DATE RUN: Dec/05/1991
GAS 1 : Argon
COMMENT1: Run 2
COMMENT2: Pt Pans

METHOD

```
No. Start Final Ramp/Iso Gas
 1     22   700     20.0   1
Sample Rate:      1.0 Sec/pt
```

Fig 12 Thermal analysis of lithium fluoride - lithium chloride - lithium bromide eutectic Run 2

Fig 13

STA 1000
STANTON REDCROFT

SMPL ID : Ternary Eut.
RUN ID : New Batch
SIZE : 12.175 mg
OPERATOR: JB

DATE RUN: Dec/05/1991
GAS 1 : Argon
COMMENT1: Run 3
COMMENT2: Pt Pans

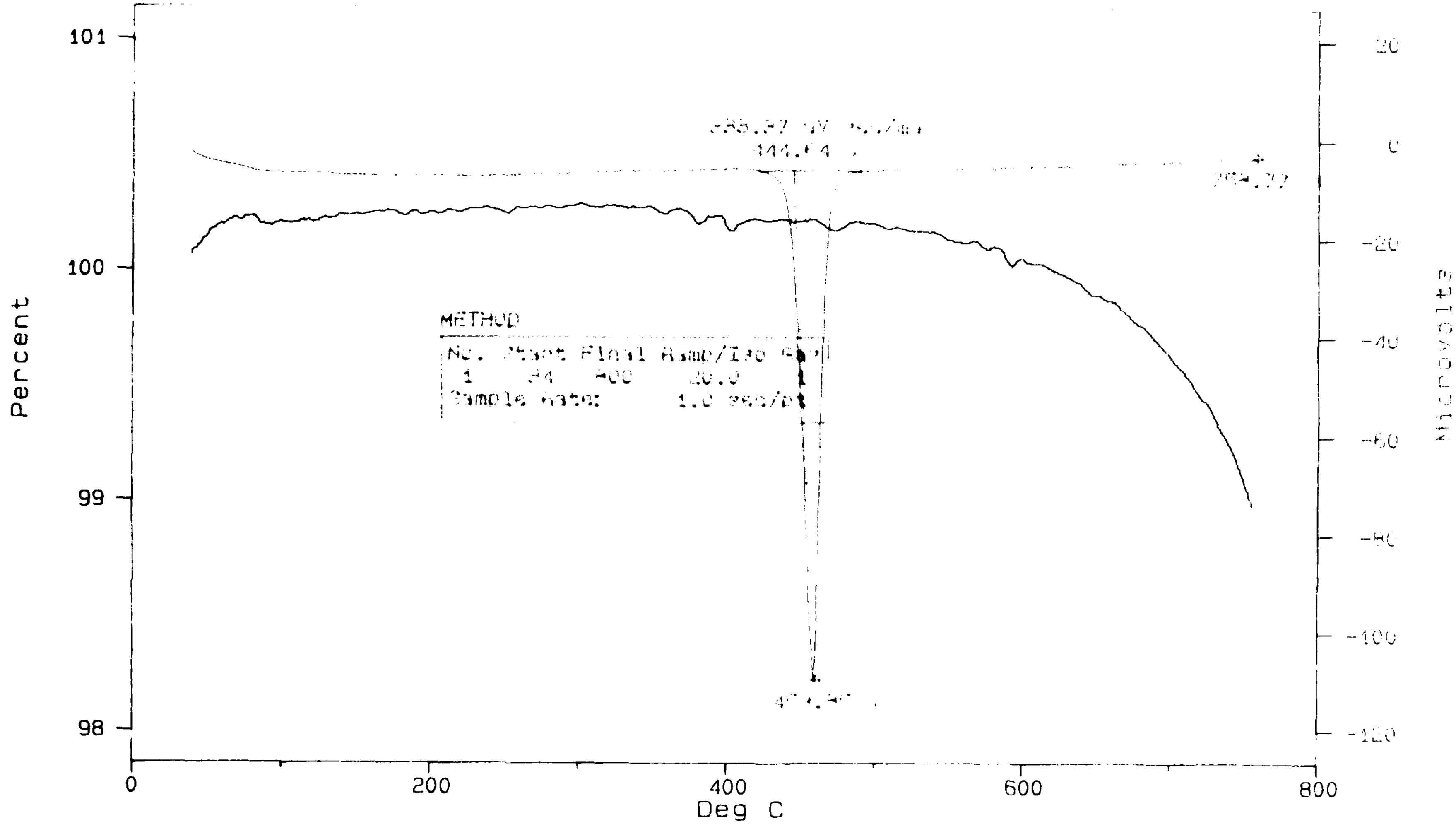


Fig 13 Thermal analysis of lithium fluoride - lithium chloride - lithium bromide eutectic Run 3

Fig 14

STA 1000
STANTON REDCROFT

SMPL ID : Ternary Eutectc
RUN ID : New Batch
SIZE : 12.018 mg
OPERATOR: JB

DATE RUN: Dec/05/1991
GAS 1 : Argon
COMMENT1: Run 4
COMMENT2: Pt pans

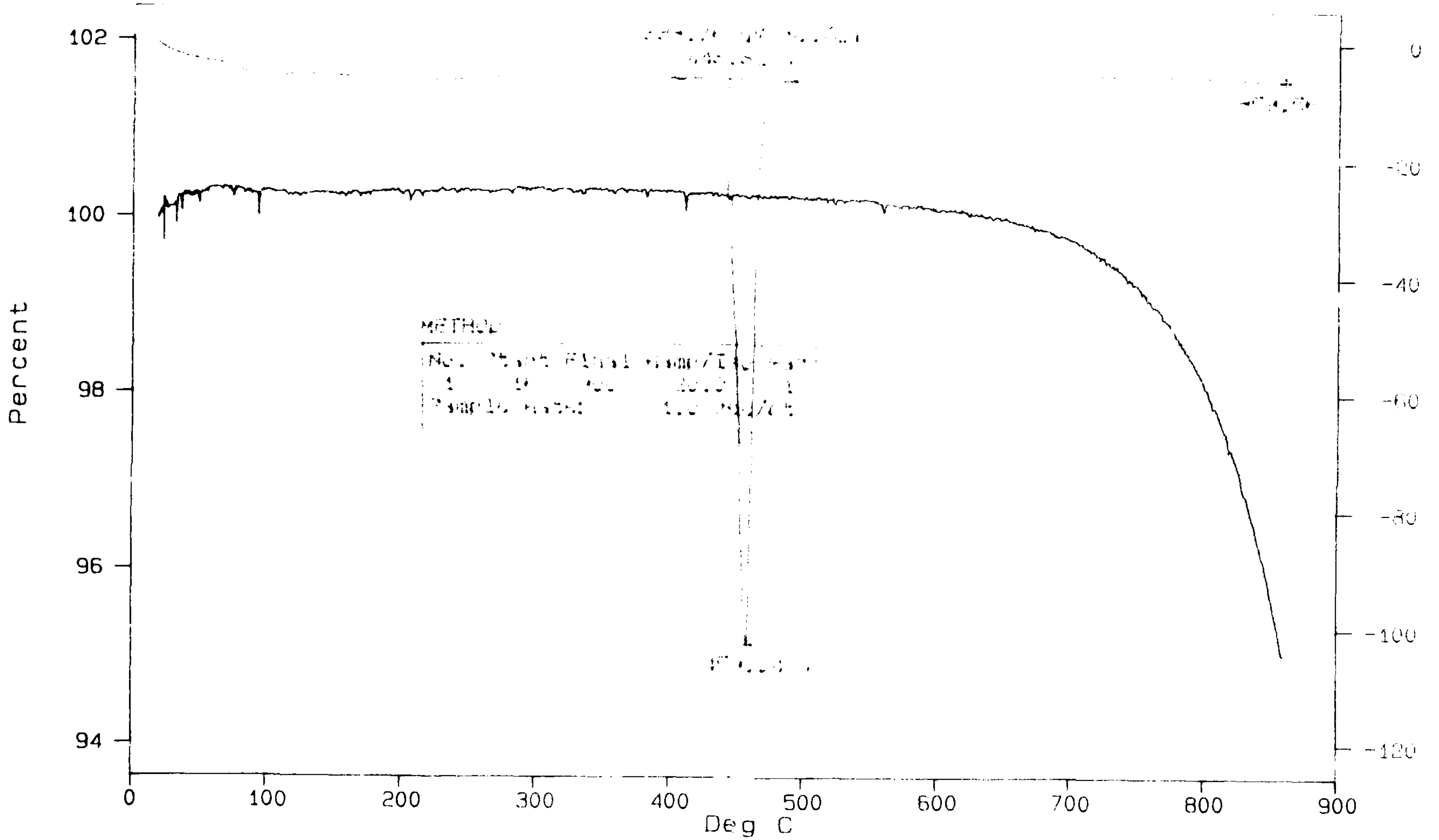


Fig 14 Thermal analysis of lithium fluoride - lithium chlori , - lithium bromide eutectic Run 4

STA 1000
STANTON REDCROFT

SMPL ID : Ternary Eutectc
RUN ID : New Batch
SIZE : 11.390 mg
OPERATOR: JB

DATE RUN: Dec/05/1991
GAS 1 : Argon
COMMENT1: Run 5
COMMENT2: Pt Pans

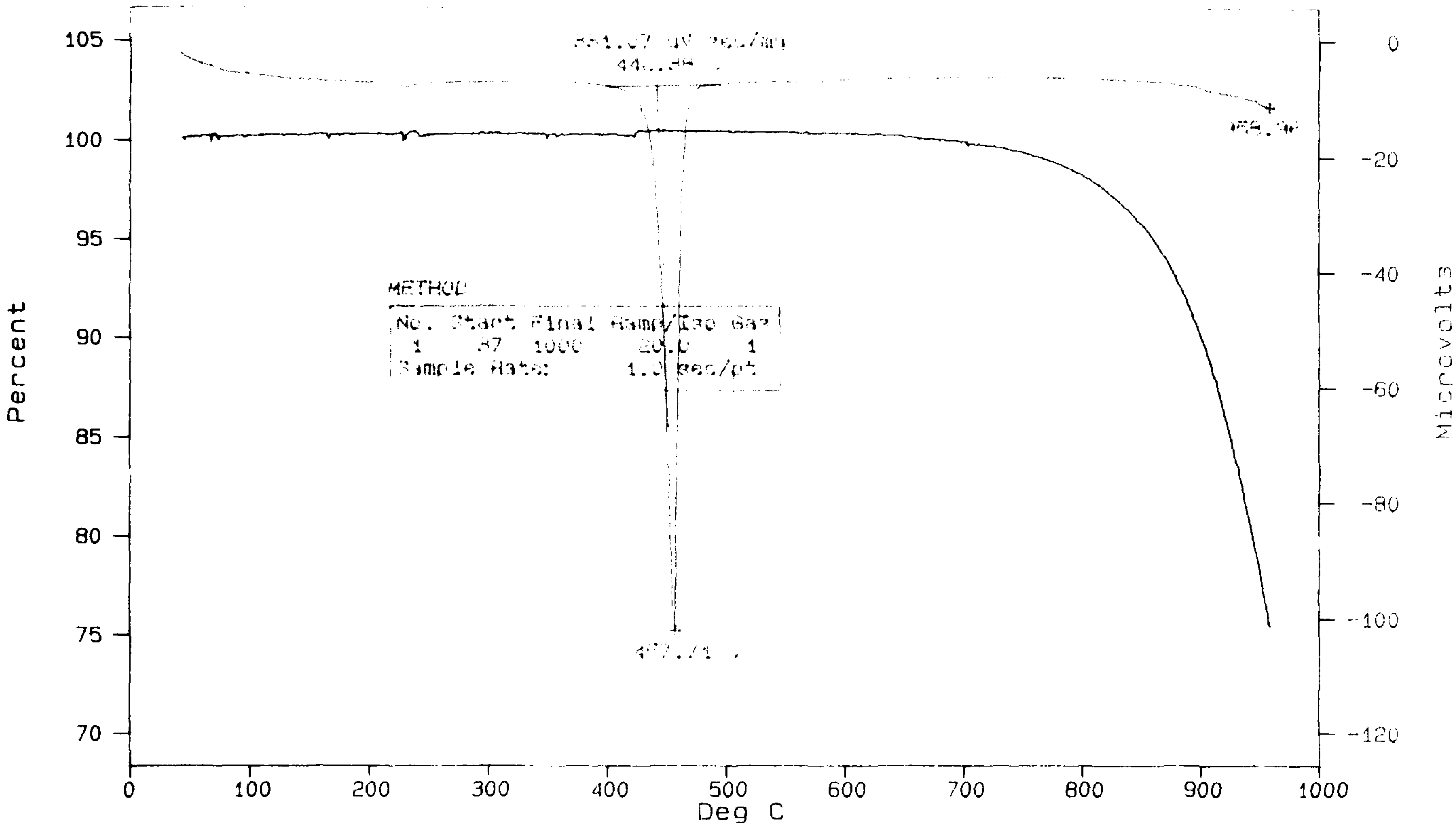
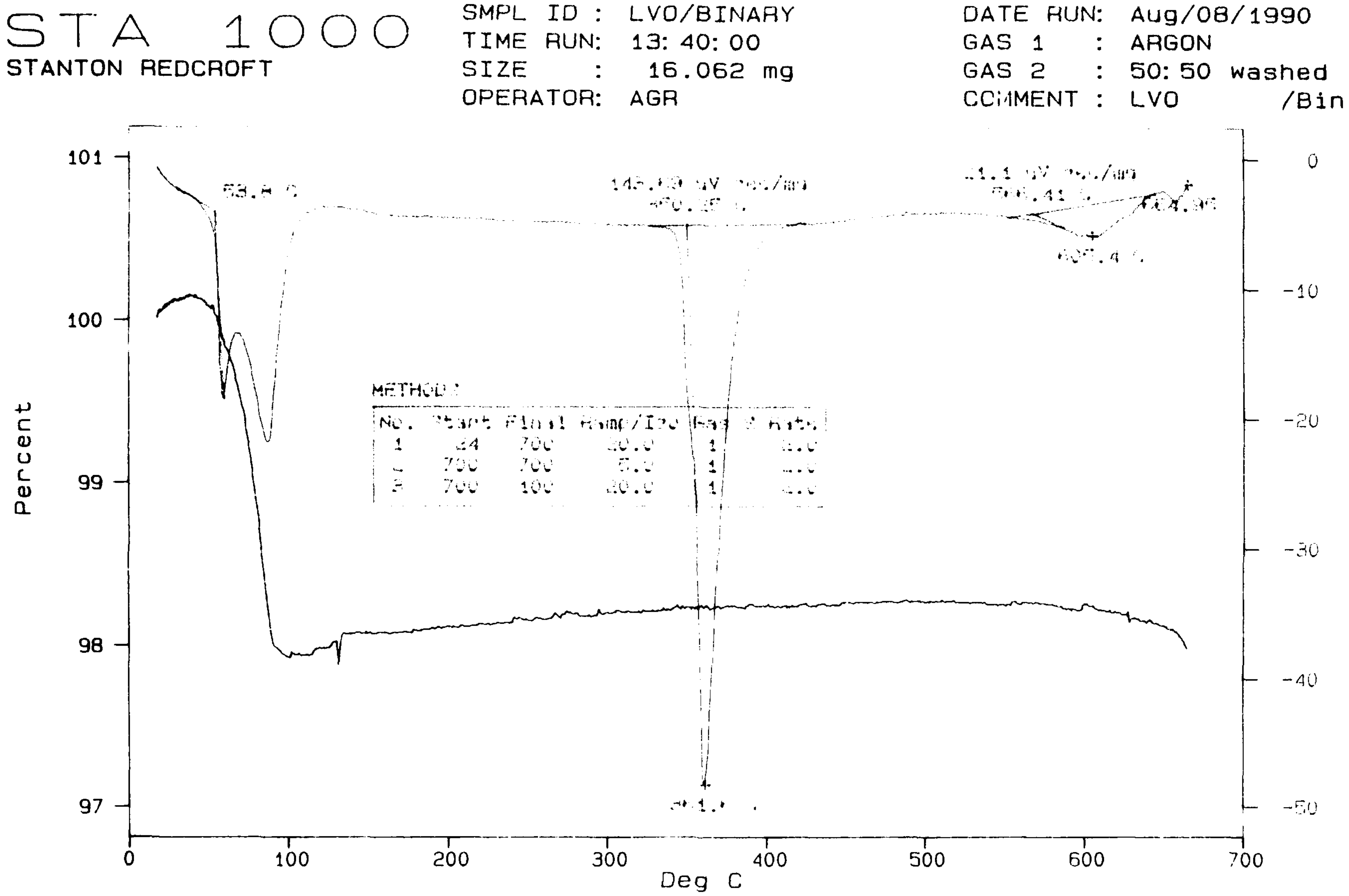


Fig 15 Thermal analysis of lithium fluoride - lithium chloride - lithium bromide eutectic Run 5



STA 1000
STANTON REDCROFT

SMPL ID : LVO/BINARY
TIME RUN: 13: 40: 00
SIZE : 16.062 mg
OPERATOR: AGR

DATE RUN: Aug/08/1990
GAS 1 : ARGON
GAS 2 : 50: 50 washed
COMMENT : LVO /Bin

METHOD

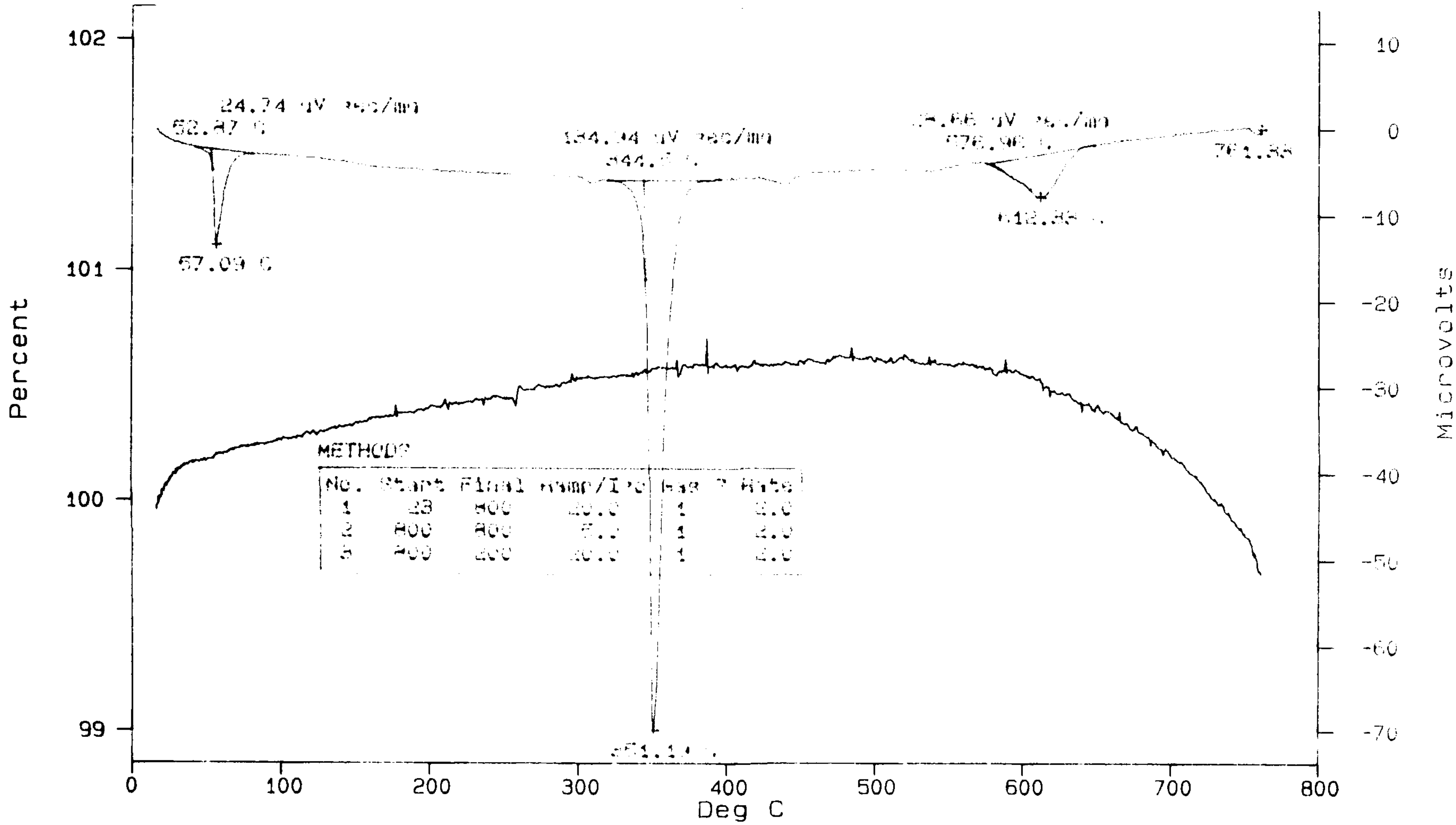
No.	Start	Final	Ramp/Iso	Gas	Rate
1	24	700	[illegible]	1	[illegible]
[illegible]	700	700	5.0	1	[illegible]
3	700	100	[illegible]	1	[illegible]

Fig 16 Thermal analysis of LVO / binary eutectic mixture Run 1

STA 1000
STANTON REDCROFT

SMPL ID : LVO/BINARY
TIME RUN: 15: 47: 00
SIZE : 15.430 mg
OPERATOR: AGR

DATE RUN: Aug/08/1990
GAS 1 : ARGON
GAS 2 :
COMMENT : REPEAT



METHODS

No.	Start	Final	Ramp/Iso	Gas	Rate
1	23	800	20.0	1	2.0
2	800	800	[illegible]	1	2.0
3	800	200	20.0	1	2.0

Fig 17 Thermal analysis of LVO / binary eutectic mixture Run 2

STA 1000
STANTON REDCROFT

SMPL ID : LVO/BINARY
TIME RUN: 09: 24: 00
SIZE : 15.020 mg
OPERATOR: AGR

DATE RUN: Aug/09/1990
GAS 1 : ARGON
GAS 2 :
COMMENT : 2nd REPEAT

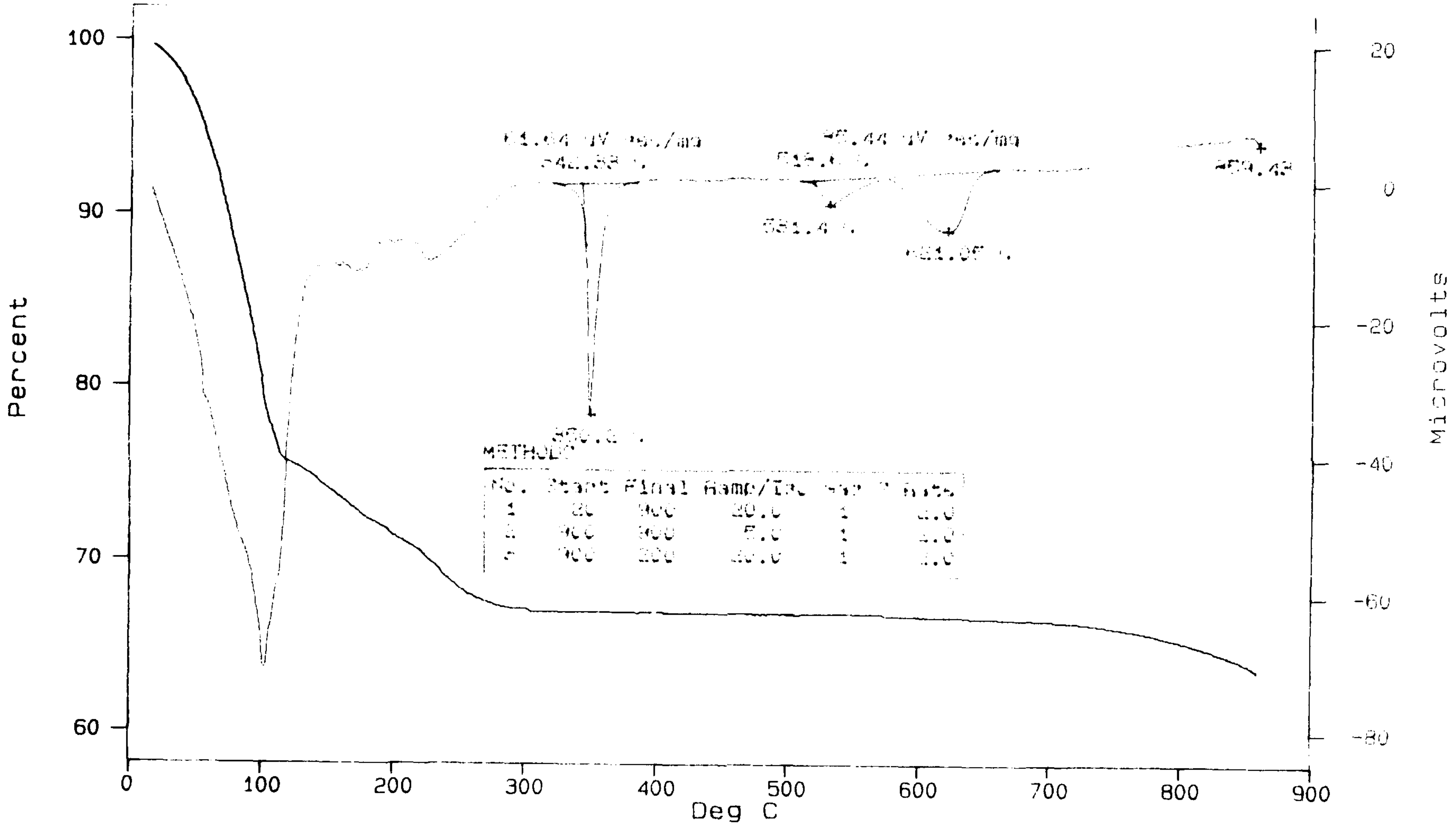
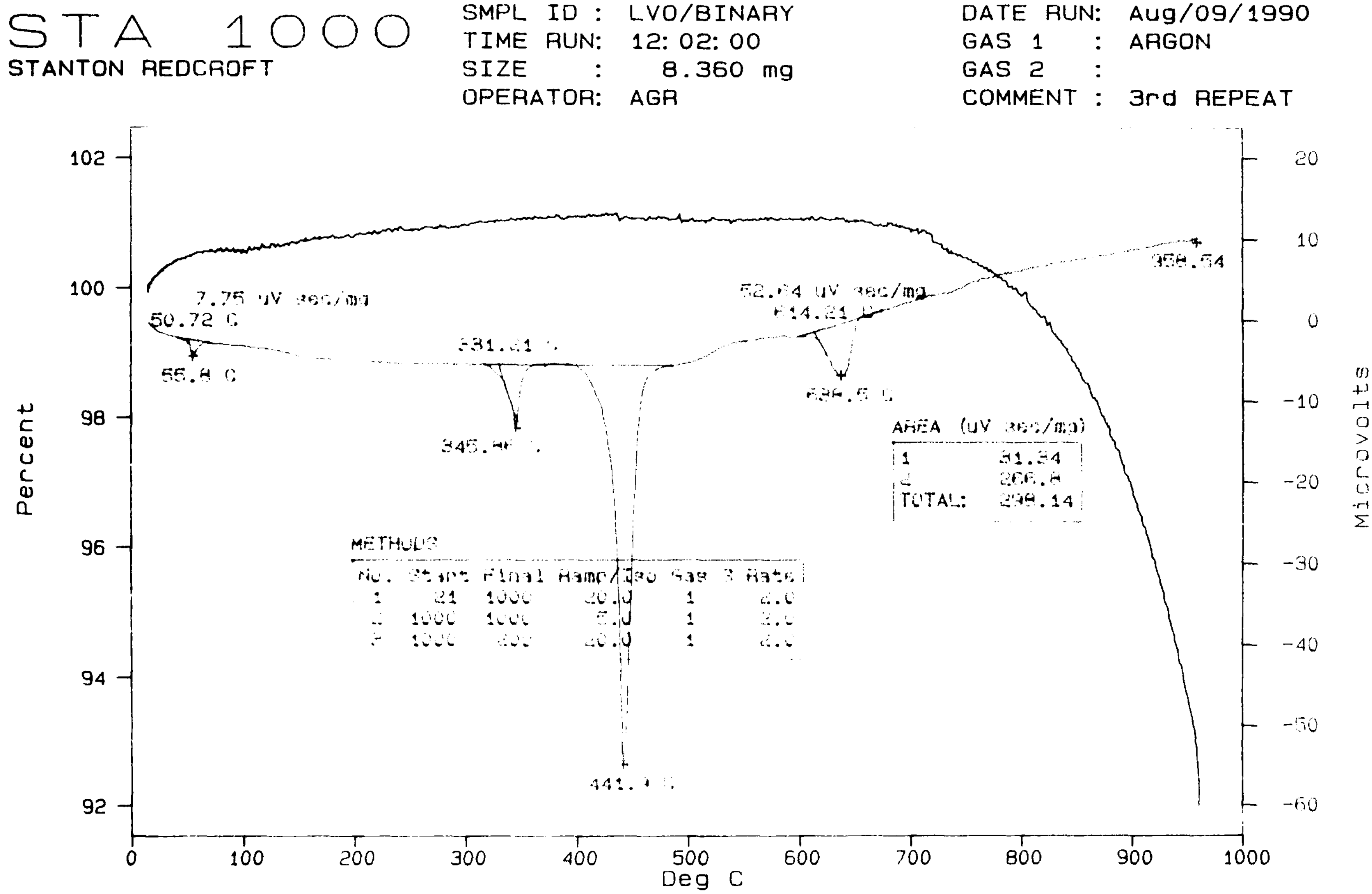


Fig 18 Thermal analysis of LVO / binary eutectic mixture Run 3



STA 1000
STANTON REDCROFT

SMPL ID : LVO/BINARY
TIME RUN: 12:02:00
SIZE : 8.360 mg
OPERATOR: AGR

DATE RUN: Aug/09/1990
GAS 1 : ARGON
GAS 2 :
COMMENT : 3rd REPEAT

METHODS

No.	Start	Final	Ramp/Iso	Gas	3 Rate
1	21	1000	20.0	1	2.0
2	1000	1000	5.0	1	2.0
3	1000	200	20.0	1	2.0

AREA (uV sec/mg)

1	31.34
2	266.8
TOTAL:	298.14

Fig 19 Thermal analysis of LVO / binary eutectic mixture Run 4

STA 1000
STANTON REDCROFT

SMPL ID : 30% Binary
RUN ID : New Batch Bin.
SIZE : 6.639 mg
OPERATOR: JB

DATE RUN: Dec/04/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 1
COMMENT2: Pt Pans

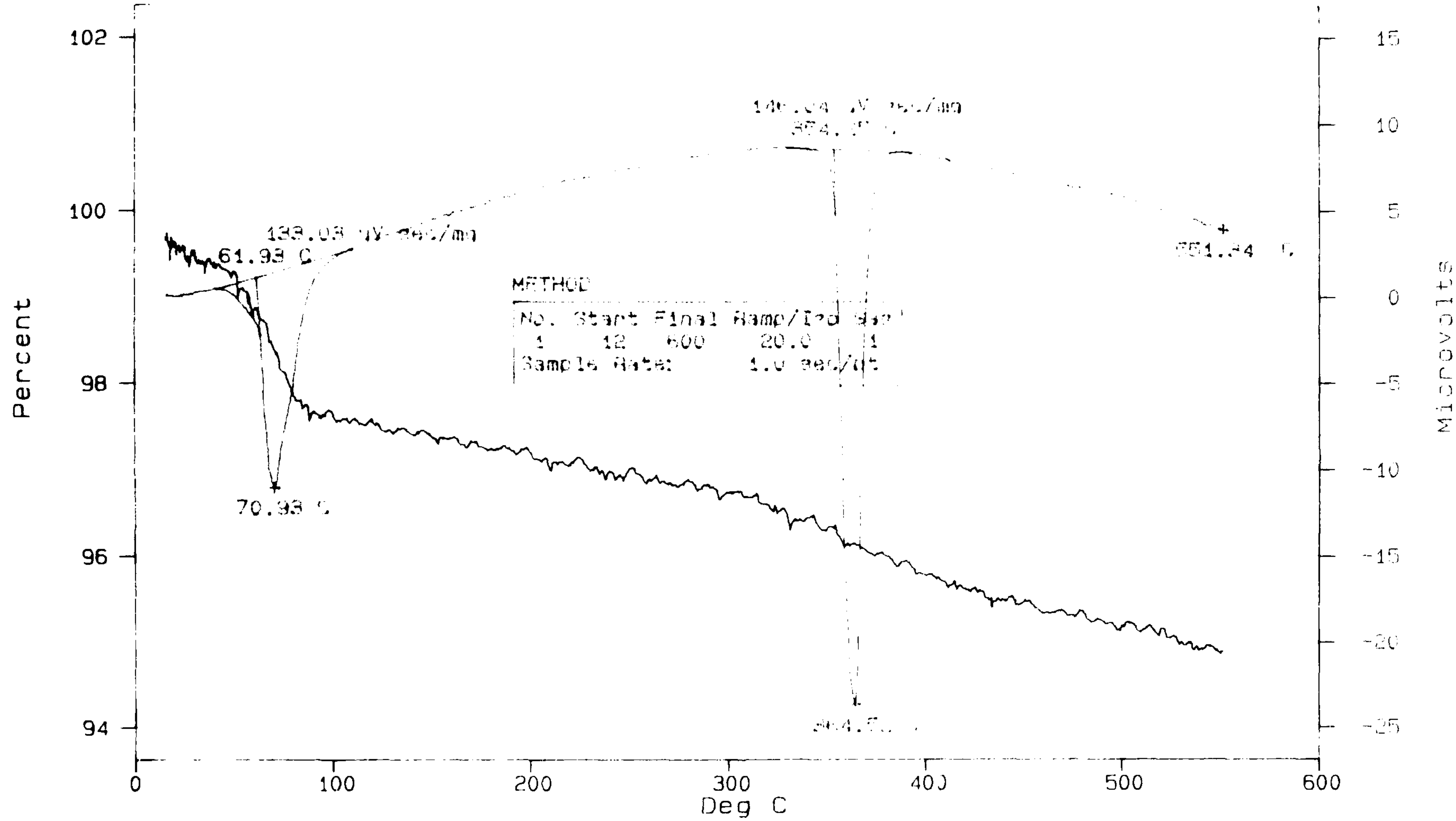


Fig 20 Thermal analysis of vanadium dioxide / binary eutectic mixture Run 1

STA 1000
STANTON REDCROFT

SMPL ID : 30% Binary
RUN ID : New Batch Bin.
SIZE : 6.496 mg
OPERATOR: JB

DATE RUN: Dec/04/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 2
COMMENT2: Pt Pans

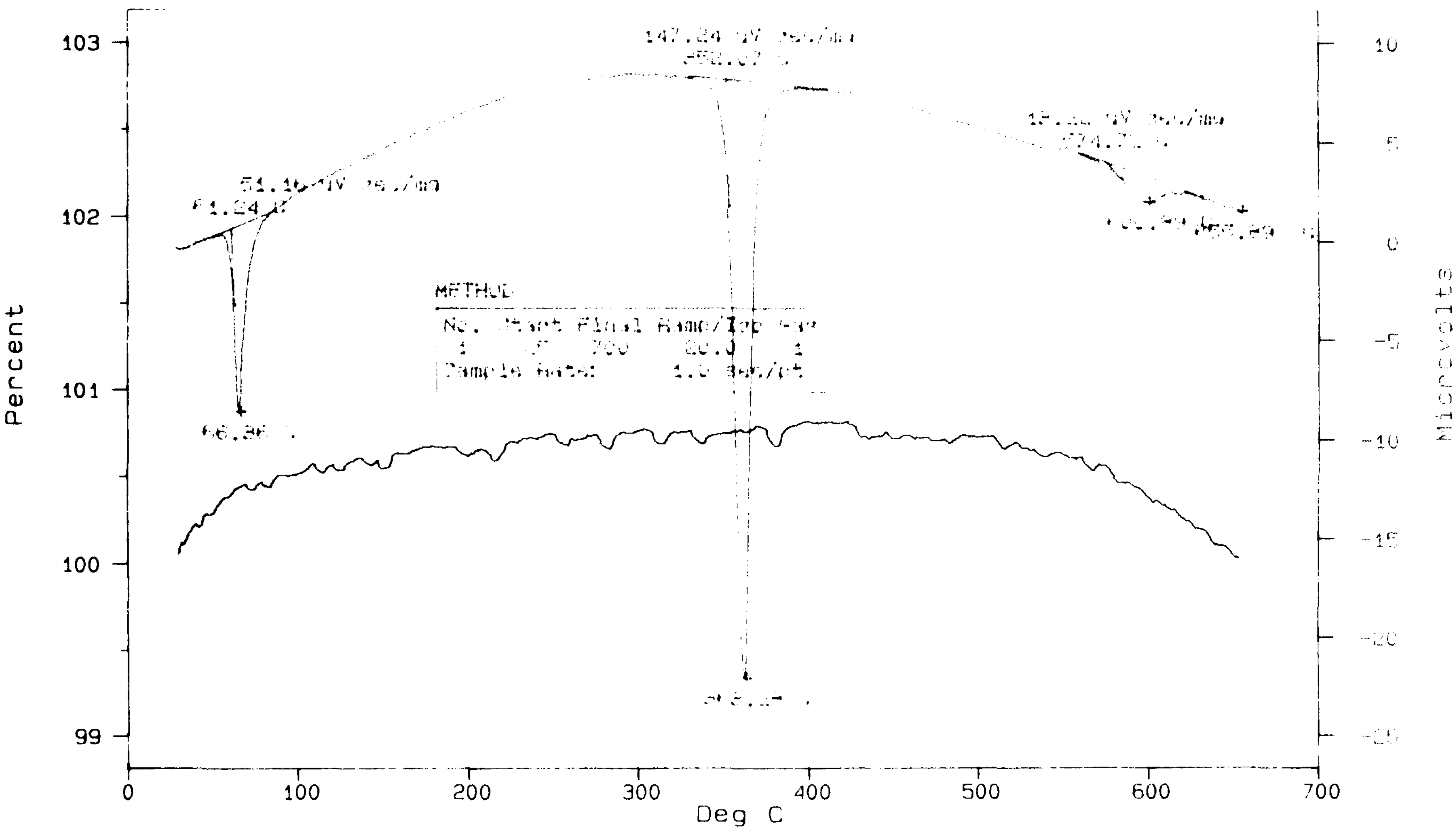
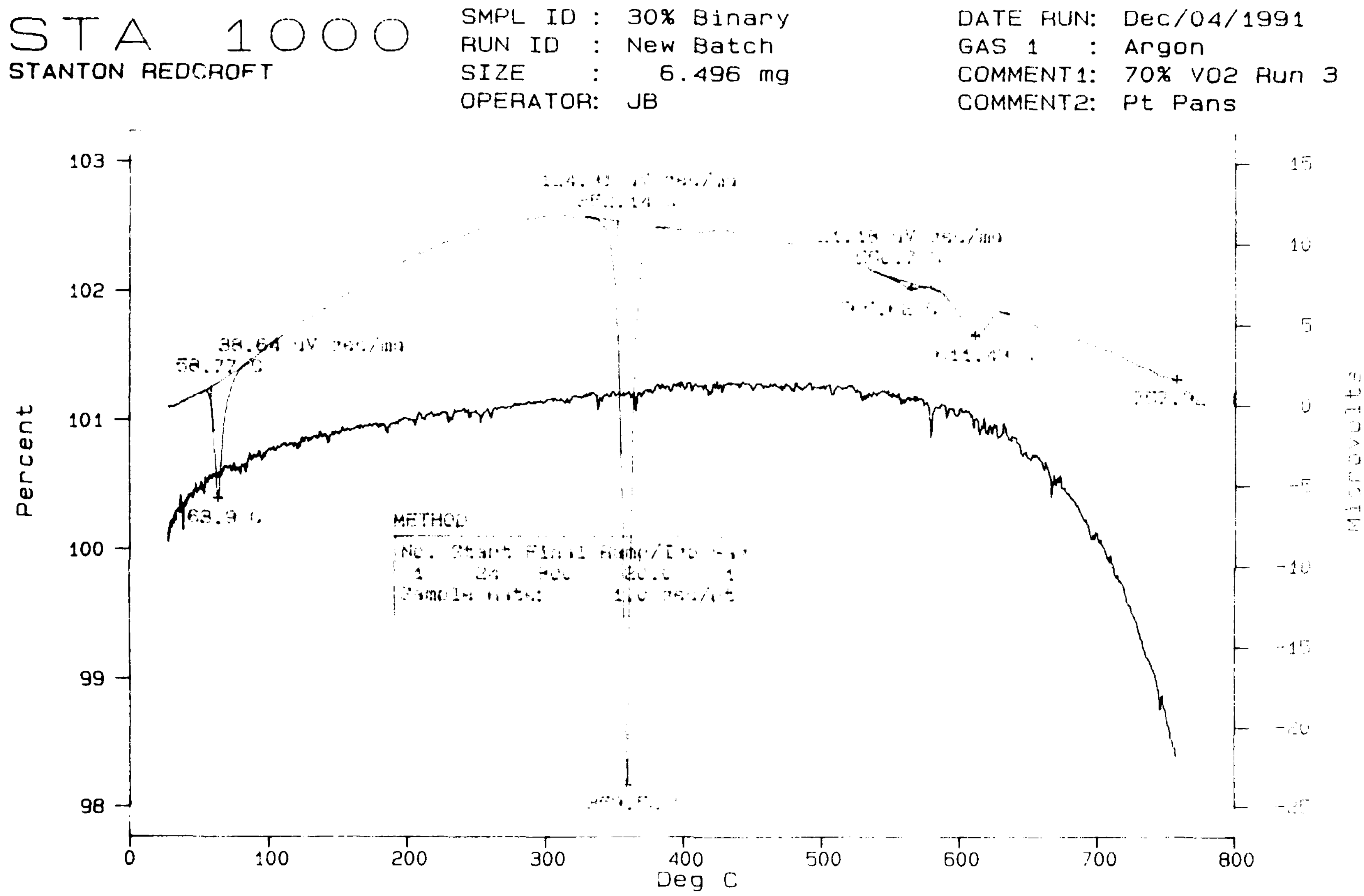


Fig 21 Thermal analysis of vanadium dioxide / binary eutectic mixture Run 2

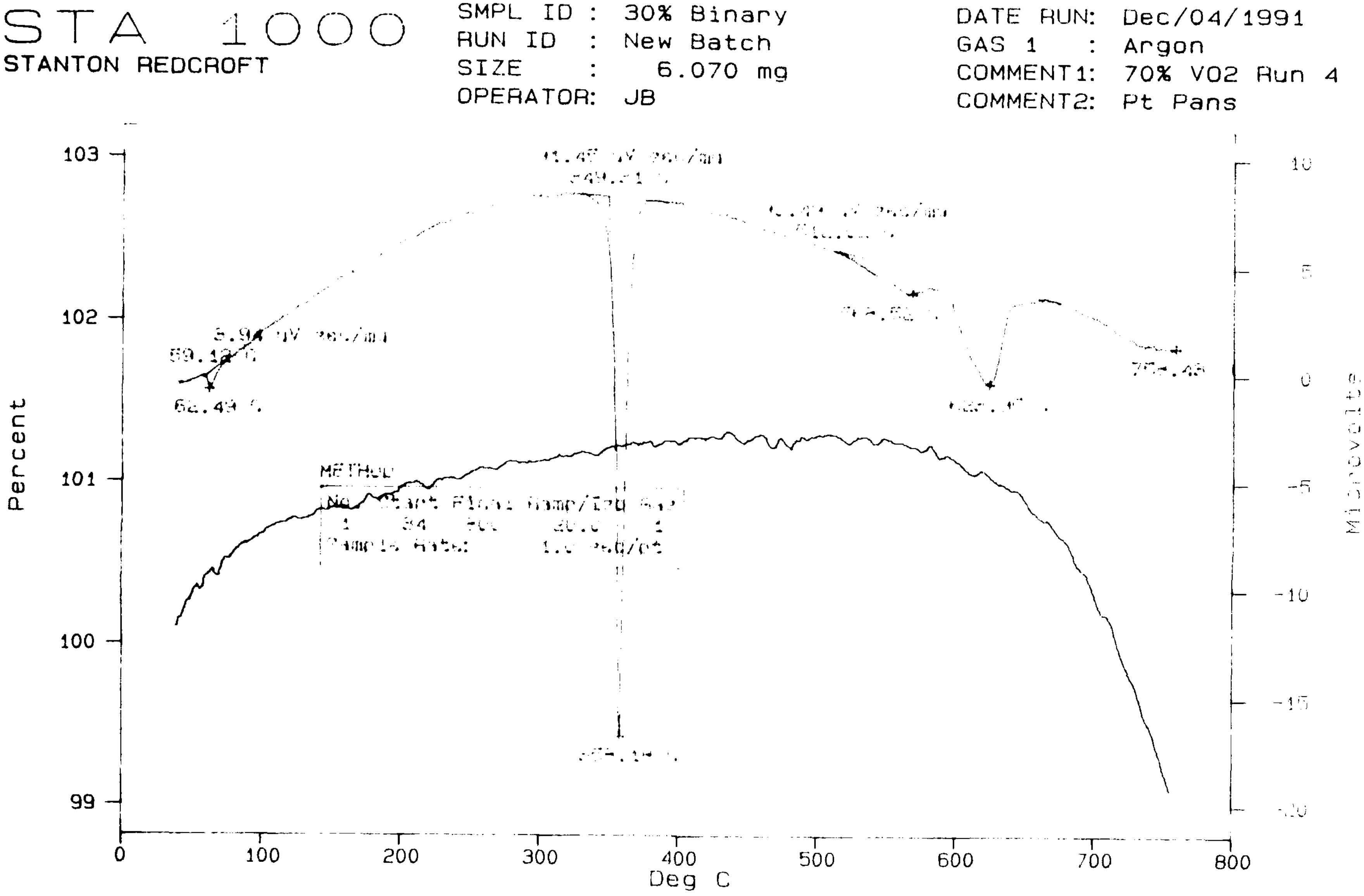


STA 1000
STANTON REDCROFT

SMPL ID : 30% Binary
RUN ID : New Batch
SIZE : 6.496 mg
OPERATOR: JB

DATE RUN: Dec/04/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 3
COMMENT2: Pt Pans

Fig 22 Thermal analysis of vanadium dioxide / binary eutectic mixture Run 3



STA 1000
STANTON REDCROFT

SMPL ID : 30% Binary
RUN ID : New Batch
SIZE : 6.070 mg
OPERATOR: JB

DATE RUN: Dec/04/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 4
COMMENT2: Pt Pans

Fig 23 Thermal analysis of vanadium dioxide / binary eutectic mixture Run 4

STA 1000
STANTON REDCROFT

SMPL ID : 30% Ternary
RUN ID : New Batch
SIZE : 5.650 mg
OPERATOR: JB

DATE RUN: Dec/06/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 1
COMMENT2: Pt Pans

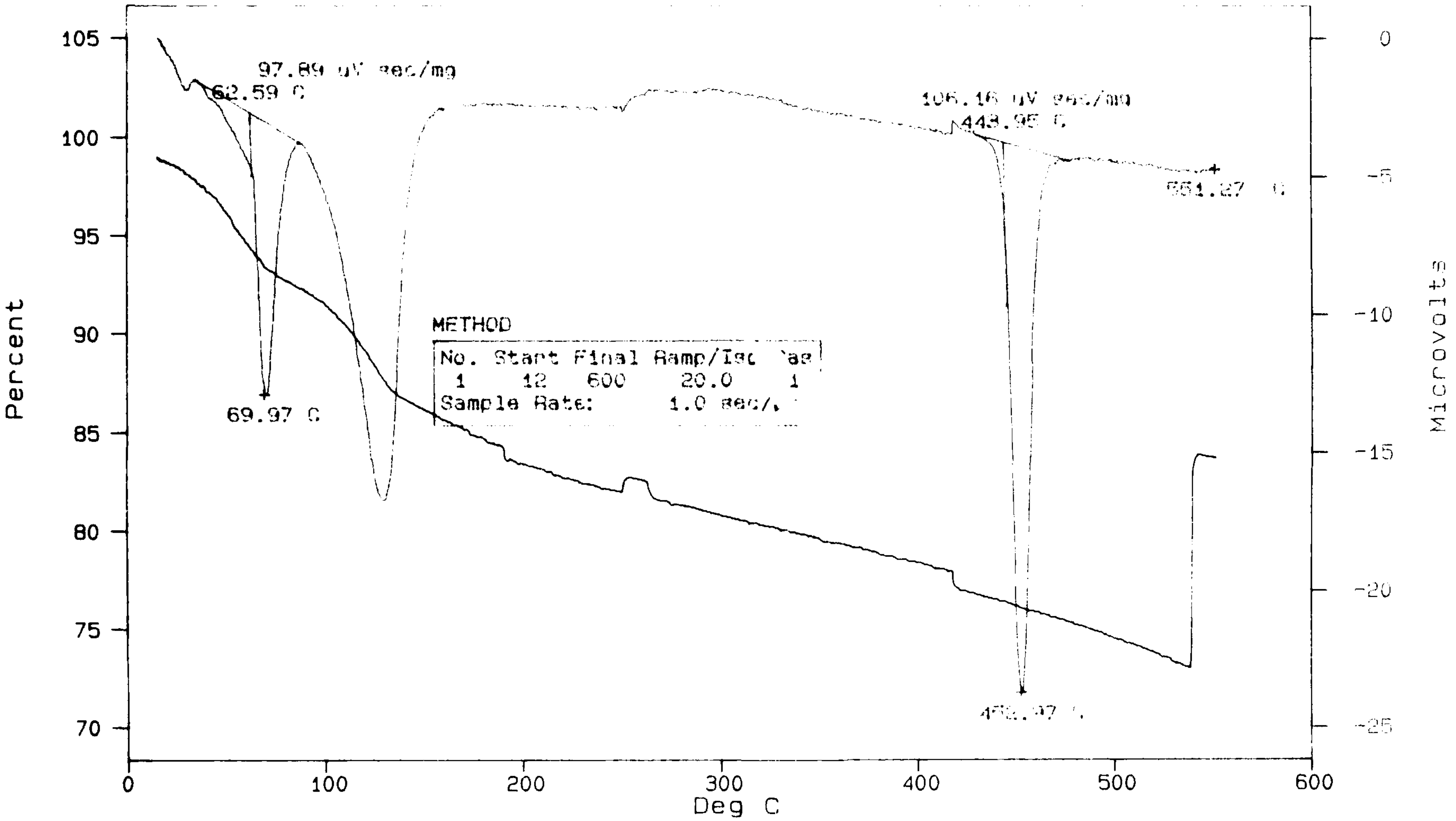
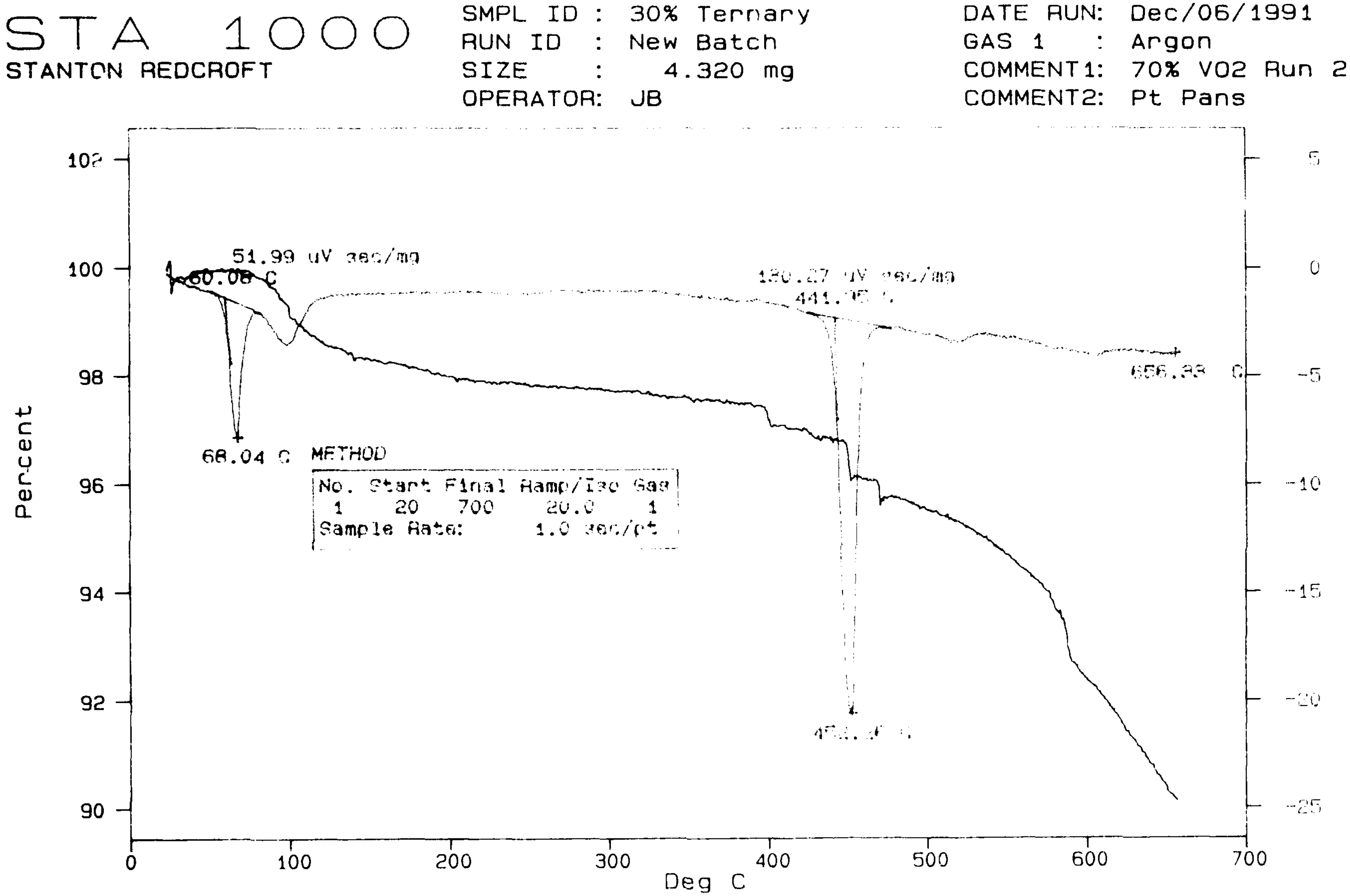


Fig 24 Thermal analysis of vanadium dioxide / ternary eutectic mixture Run 1



STA 1000
STANTON REDCROFT

SMPL ID : 30% Ternary
RUN ID : New Batch
SIZE : 4.320 mg
OPERATOR: JB

DATE RUN: Dec/06/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 2
COMMENT2: Pt Pans

METHOD

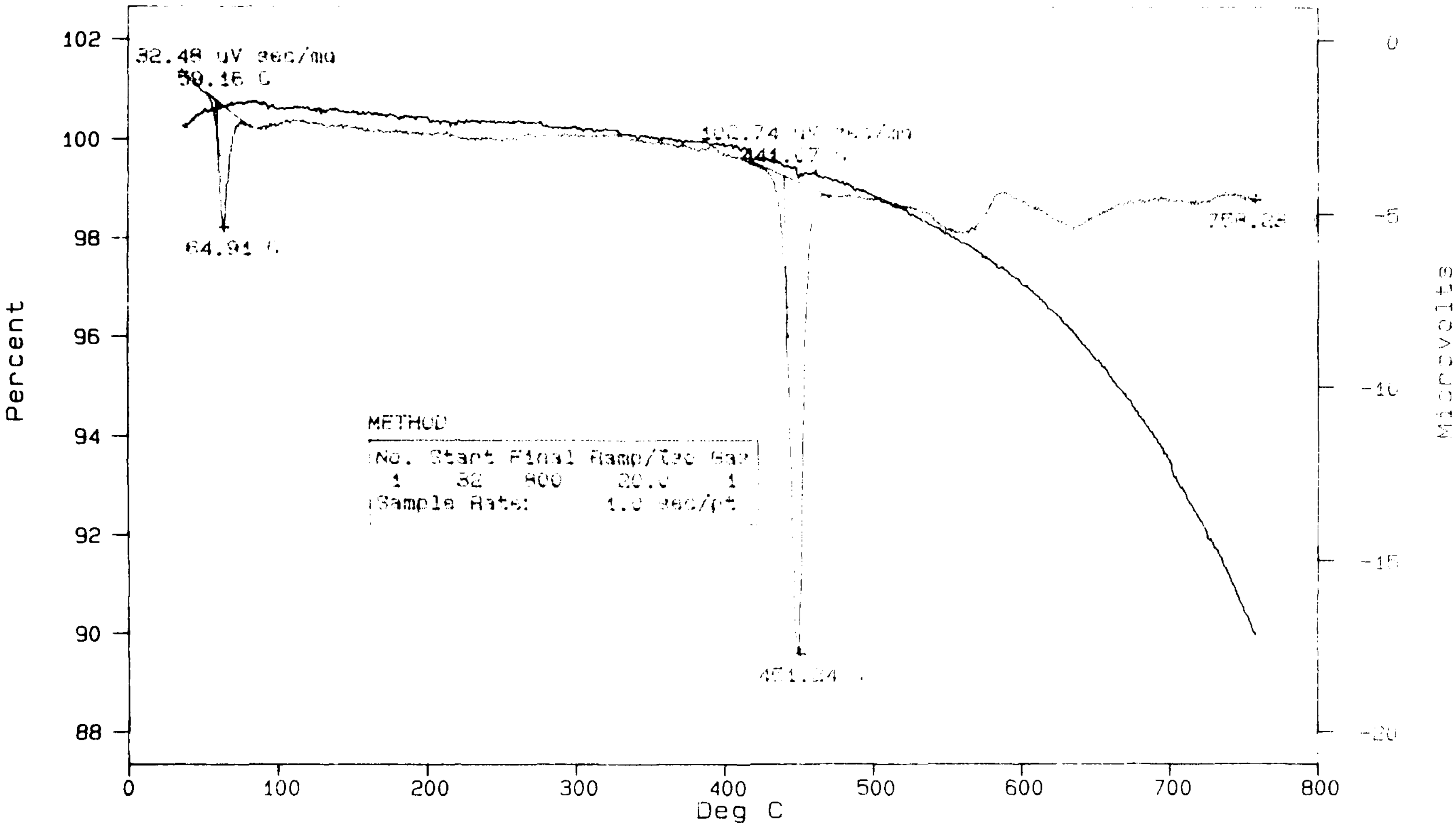
No.	Start	Final	Ramp/Iso	Gas
1	20	700	20.0	1
Sample Rate:			1.0 sec/pt	

Fig 25 Thermal analysis of vanadium dioxide / ternary eutectic mixture Run 2

STA 1000
STANTON REDCROFT

SMPL ID : 30% Ternary
RUN ID : New Batch
SIZE : 3.880 mg
OPERATOR: JB

DATE RUN: Dec/06/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 3
COMMENT2: Pt Pans



METHOD

No.	Start	Final	Ramp/Deg	Gas
1	32	800	20.0	1

Sample Rate: 1.0 sec/pt

Fig 26 Thermal analysis of vanadium dioxide / ternary eutectic mixture Run 3

STA 1000
STANTON REDCROFT

SMPL ID : 30% Ternary
RUN ID : New Batch
SIZE : 3.500 mg
OPERATOR: JB

DATE RUN: Dec/06/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 4
COMMENT2: Pt Pans

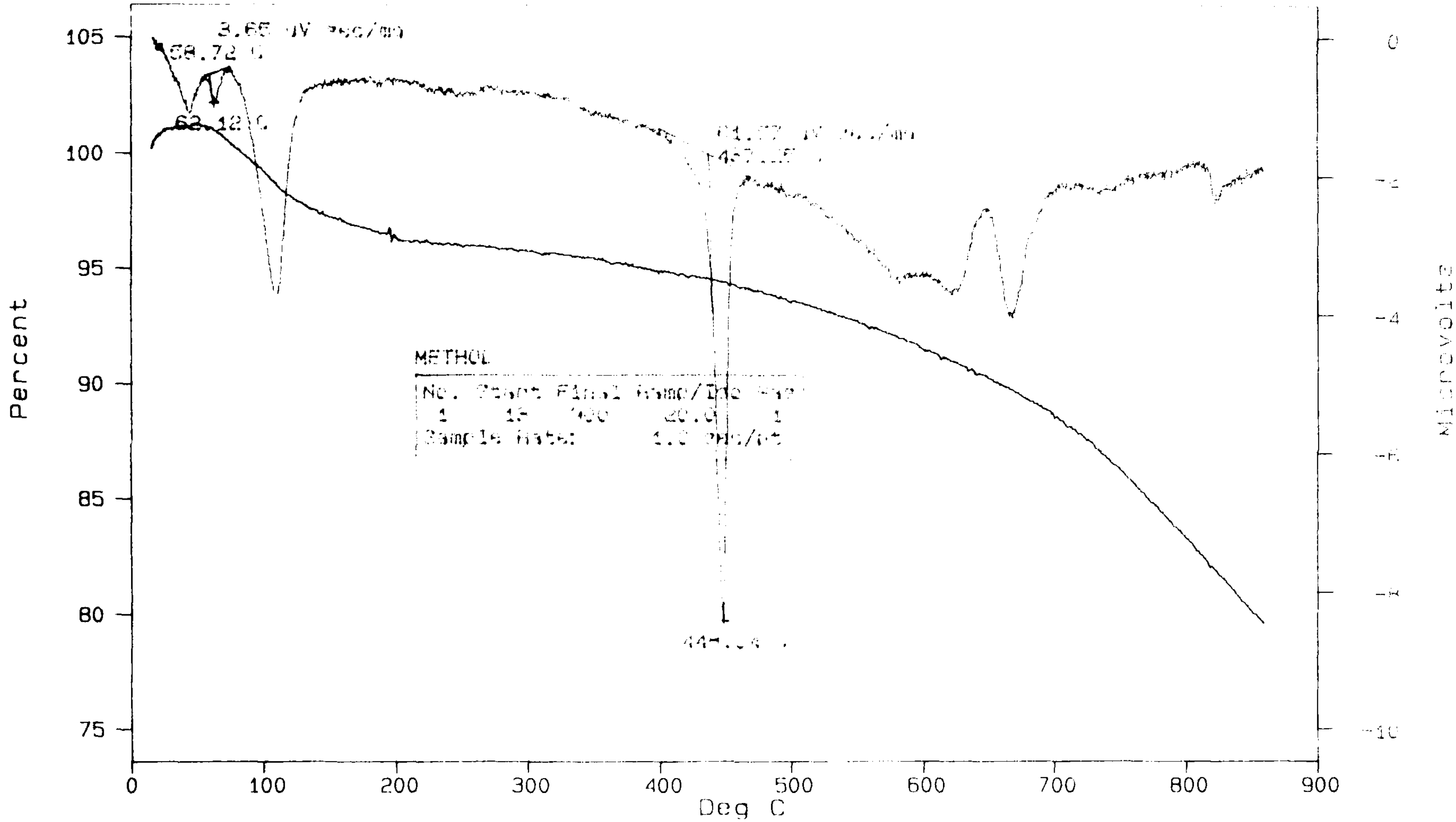
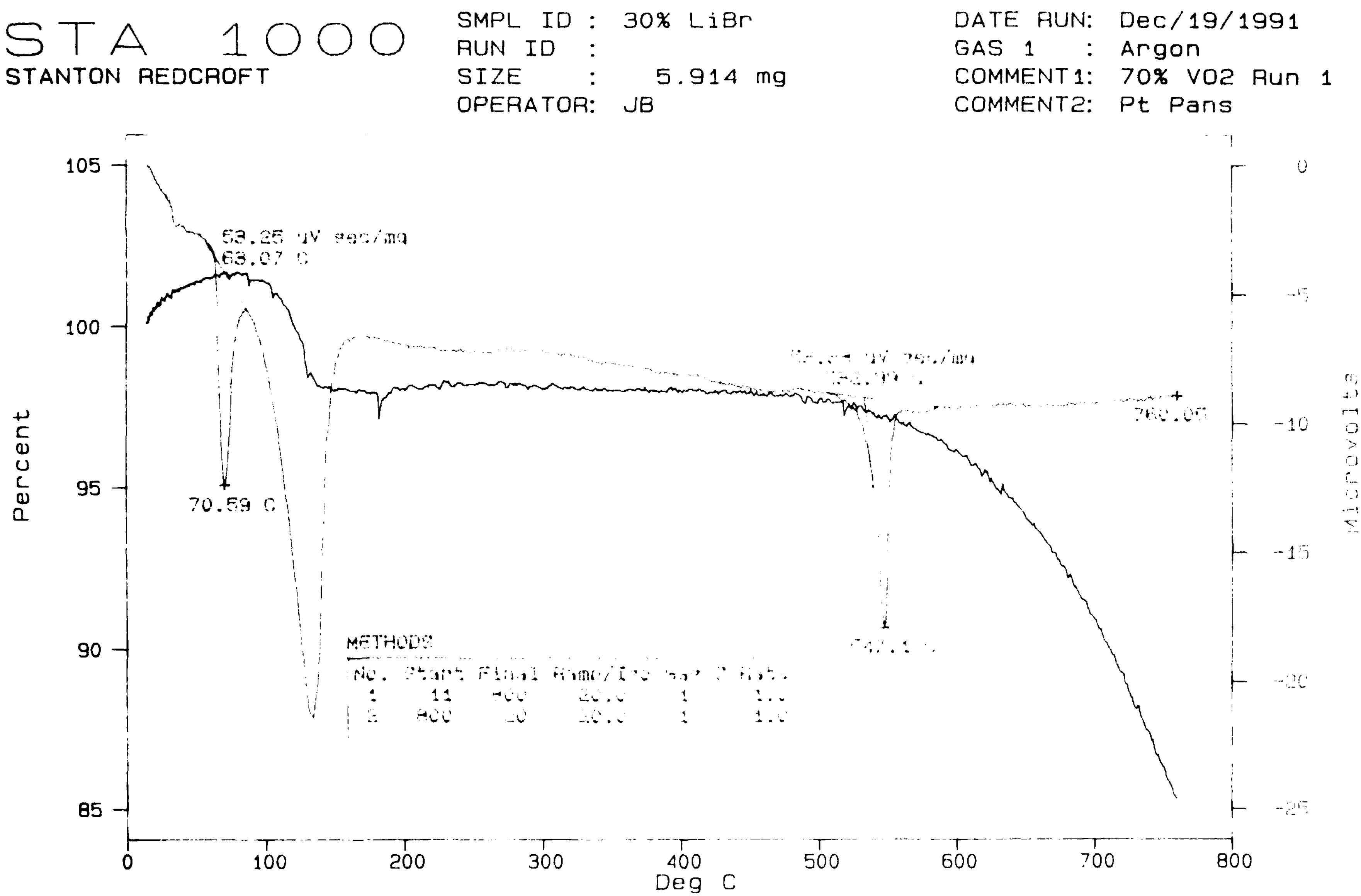


Fig 27 Thermal analysis of vanadium dioxide / ternary eutectic mixture Run 4



STA 1000
STANTON REDCROFT

SMPL ID : 30% LiBr
RUN ID :
SIZE : 5.914 mg
OPERATOR: JB

DATE RUN: Dec/19/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 1
COMMENT2: Pt Pans

Fig 28 Thermal analysis of vanadium dioxide / lithium bromide mixture Run 1

Fig 29

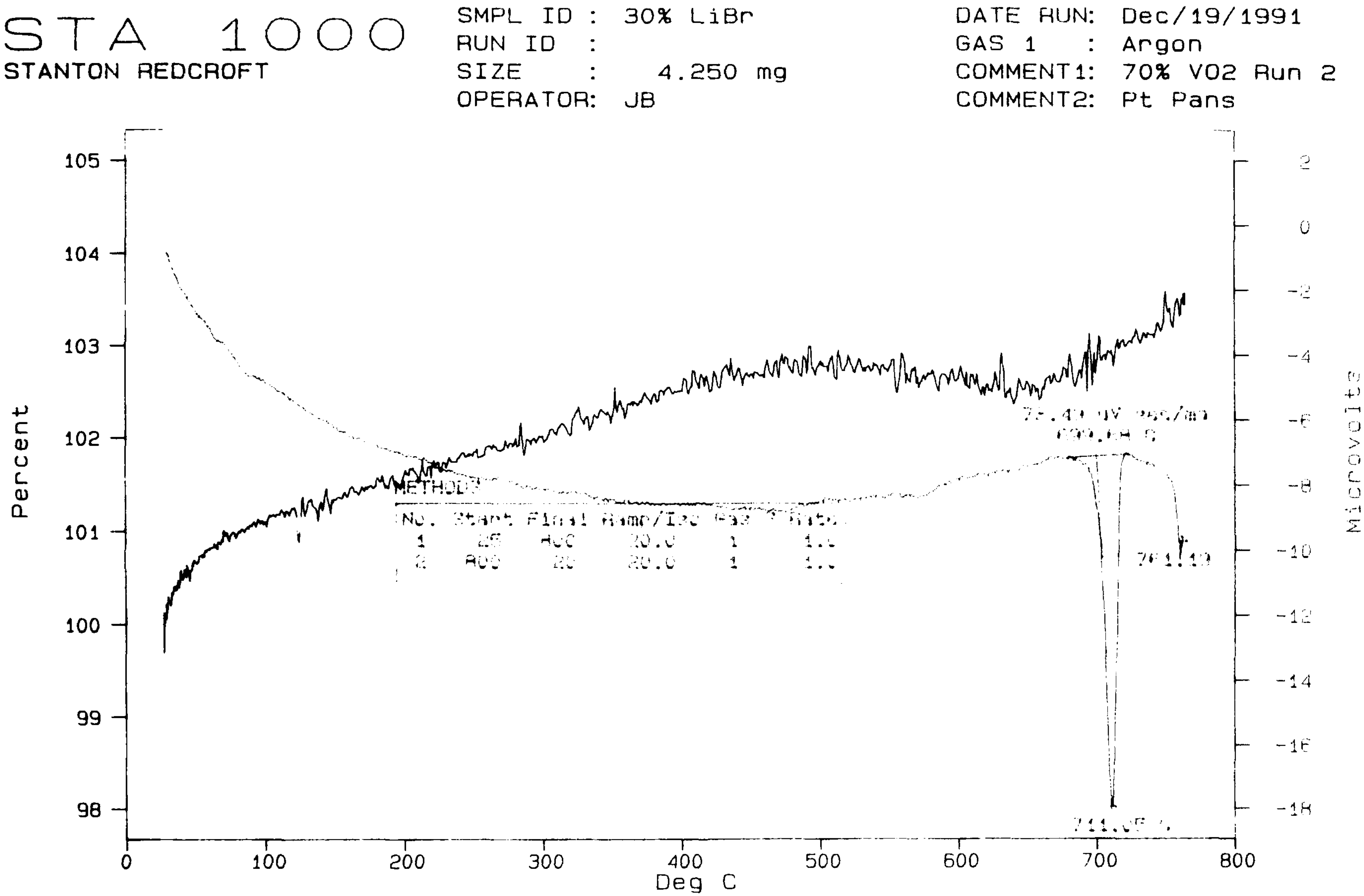


Fig 29 Thermal analysis of vanadium dioxide / lithium bromide mixture Run 2

STA 1000
STANTON REDCROFT

SMPL ID : 30% LiCl
RUN ID : 700C 20C/Min.
SIZE : 9.679 mg
OPERATOR: JB

DATE RUN: Dec/20/1991
GAS 1 : Argon
COMMENT1: 70% VO2 Run 1
COMMENT2: Pt Pans

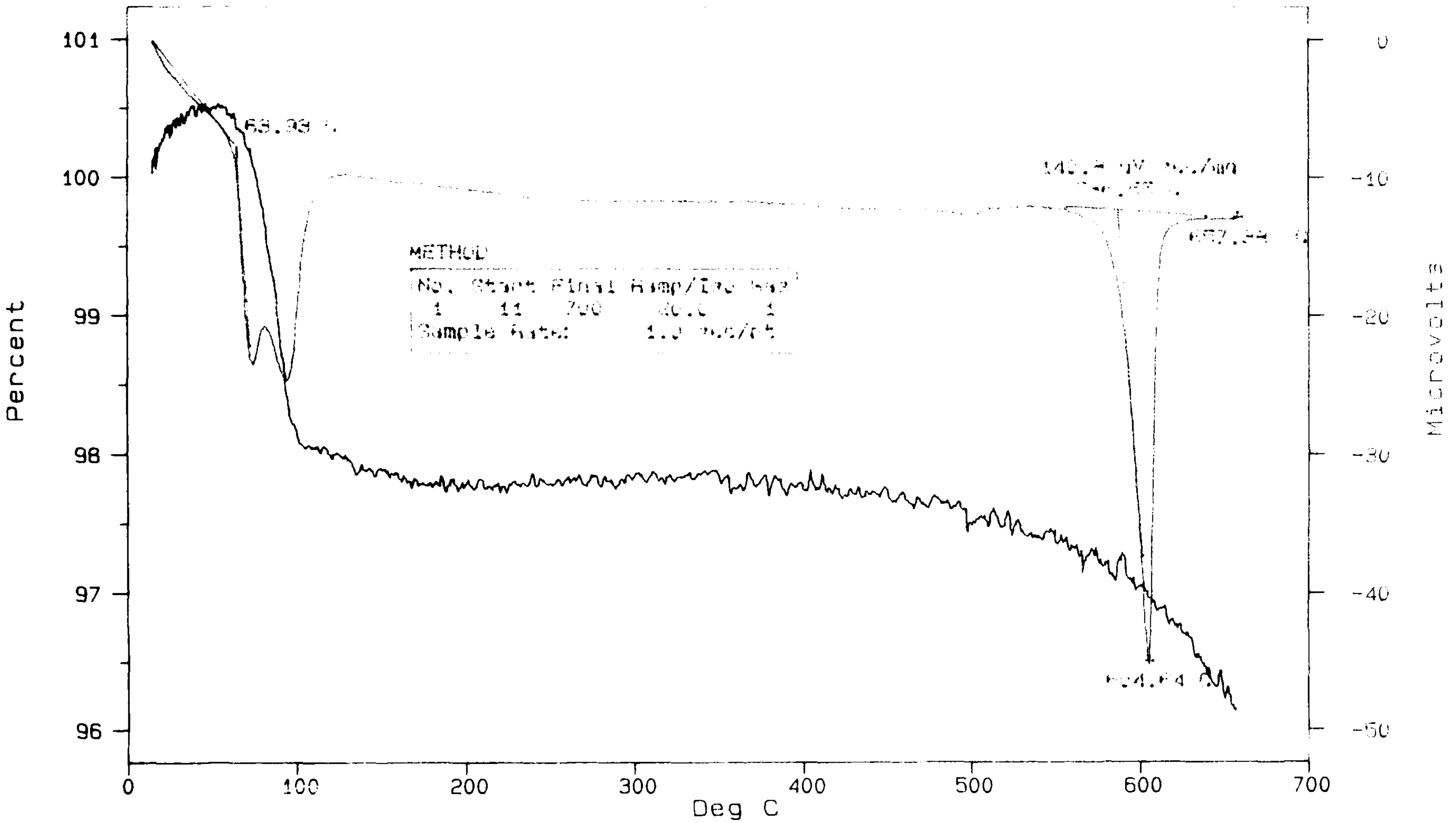


Fig 30 Thermal analysis of vanadium dioxide / lithium chloride mixture Run 1

Fig 30

Fig 31

STA 1000
STANTON REDCROFT

SMPL ID : 30% LiCl
RUN ID : 700C 20C/min.
SIZE : 8.855 mg
OPERATOR: JB

DATE RUN: Dec/20/1991
GAS 1 : Argon
COMMENT1: 70% V02 Run 2
COMMENT2: Pt Pans

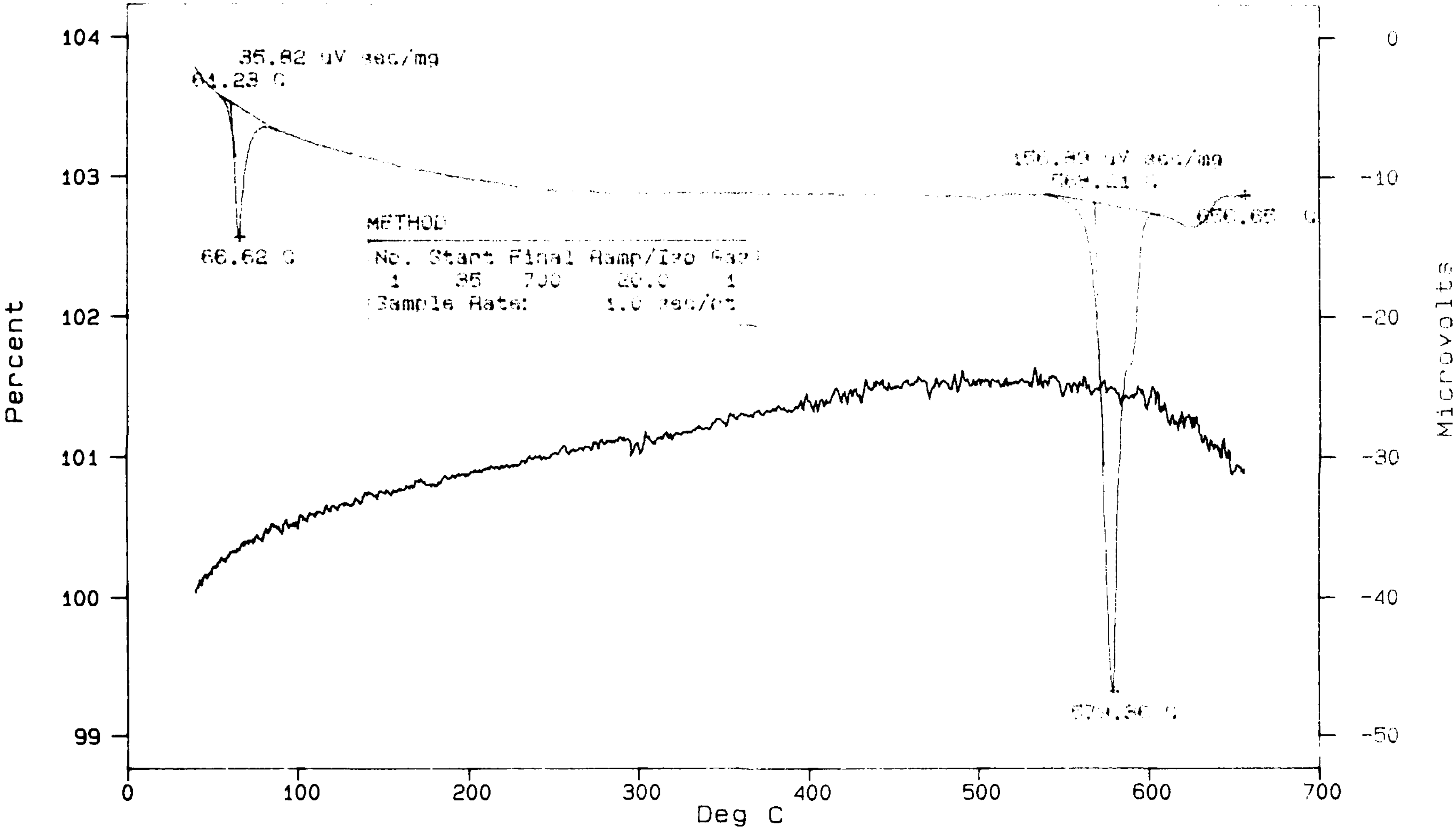


Fig 31 Thermal analysis of vanadium dioxide / lithium chloride mixture Run 2

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REPORT DOCUMENTATION PAGE

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5. DRIC Code for Originator 7673000W	6. Originator (Corporate Author) Name and Location DRA Farnborough, Hampshire, GU14 6TD
5a. Sponsoring Agency's Code F09C9HXX	6a. Sponsoring Agency (Contract Authority) Name and Location DDOR3(Air)

7. Title
Thermal Stability of Lithium Vanadium Oxide (LVO), γ-Lithium Vanadium Bronze (γ-LiV_2O_5) and Vanadium Dioxide (VO_2) Thermal Battery Cathode Materials

7a. (For Translations) Title in Foreign Language

7b. (For Conference Papers) Title, Place and Date of Conference

8. Author 1, Surname, Initials	9a. Author 2	9b. Authors 3,4 ...	10. Date	Pages	Refs
Ritchie, A.G.	Bryce, J.C.		July 1992		15

11. Contract Number	12. Period	13. Project	14. Other Reference Nos. Materials & Structures 357

15. Distribution statement

(a) Controlled by –

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16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)

Thermal battery cathode.

17. Abstract

Thermal analysis of LVO has shown that it has limited thermal stability, possibly accounting for the failure of some thermal batteries with LVO cathodes. Its minor component, γ-LiV_2O_5, melts at temperatures which could be reached during thermal battery activation. The major component of LVO, VO_2, is thermally stable on its own, but can react with lithium chloride-potassium chloride binary eutecticwhen heated for prolonged periods above 700°C, though VO_2/binary eutectic mixtures should be sufficiently stable for use in thermal batteries.

F5910/1