Cryoscopic and Compatibility Studies
of Molten Quaternary Ammonium Salts

A Thesis
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the Chancellor’s Scholars Council
of Pembroke State University

by

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Advisor’s Approval---Paul A Flowers---

Date---24 Nov 1993---

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Cryoscopic Studies in Molten Quaternary Alkylammonium Bromides

Abstract

Cryoscopic constants (K_f) were experimentally determined using a differential thermal analyzer (DTA) for a series of four tetra-n-alkylammonium bromides. Compatibility tests between this series of salts and various structural components of the testing apparatus were performed. $(n\text{-}C_5H_{11})_4Br$ was found to have a value of 12.2 °C/m, and $(n\text{-}C_7H_{13})_4Br$ was found to have a value of 31.7 °C/m. Irreproducible results prevented the determination of K_f for $(n\text{-}C_6H_{13})_4Br$ or the salt $(n\text{-}C_4H_9)_4Br$. It was found that none of the elements of the experimental apparatus reacted with the salts. The materials tested were Teflon, Viton, Pb and CaF_2.

Introduction

This research project involves the cryoscopic studies required as a precursor to infrared spectroscopic analysis of solubility and partition equilibria in binary molten salt/supercritical fluid mixtures. The properties of molten salts make them an important class of nonaqueous solvents. They often possess large decomposition potentials and high conductivities. This combination makes them attractive as solvents in electrochemistry. They are also generally transparent over a large portion of the electromagnetic spectrum. This property allows them to be useful in spectroscopic analysis. In addition to these properties

molten salts have a long history of practical application in industry and research.(2,3) Mamantov et al. discuss this further in the book "Molten Salt Chemistry".

Supercritical fluids have seen increased applications in the past ten years in analytical schemes. The utility of supercritical fluids comes from a number of properties. Supercritical fluids are essentially high pressure gases. These high pressures cause changes in physical properties such as viscosities and solute diffusion rates. These diffusion rates are between those for gases and liquids. Solvent strength may be changed by adjusting the pressure, rather than solvent concentration. This latter trait is of particular interest to researchers.

Recent work done by Wightman determined that certain ammonium salts, under high pressures of carbon dioxide or nitrous oxide, fuse at temperatures far below their standard melting points.(4) This allowed formation of thin coatings on microelectrodes. These films acted as surface modifiers allowing analysis of solutes in supercritical media. This was apparently the first time supercritical fluids and molten salts were used together in an analytical scheme. Specifically, Wightman was developing an electrochemical detection method for supercritical fluid chromatography. For advancements in this and other types of supercritical fluid analysis to occur, fundamental knowledge of mutual solubility and phase partition phenomena will be needed. As

a pre-requisite of solubility and phase experimentation, certain cryoscopic studies must be completed.

Following the cryoscopic work, solubility and partition data will be obtained from infrared spectra using the Physical Science Department's Fourier transform infrared spectrometer (FTIR) and a high-pressure optical cell(1) (See Figure 3). This cell has already been constructed at the University of North Carolina machine shop. FTIR was chosen for a number of reasons. It does not have some of the limitations that similar UV/VIS instruments have. It can be operated at a wide range of temperatures and the specific salts being used are easily identified in the infrared spectral range. The cell is constructed in such a way as to allow the more dense molten salt to settle on the bottom. The optical window at the bottom of the cell will provide the access for infrared spectral monitoring that is necessary. The cryoscopic data will be utilized in addition to the infrared spectra to determine the partition coefficients as a function of pressure and temperature. A knowledge of these partition equilibria may also further the application of supercritical fluid extraction (SFE). This procedure would involve the extraction of chemical species from their native material such as ore, food or soil. It is hoped that these data can then be used to determine the partition equilibria for some relevant environmental toxins.(1)

Before equilibrium partitioning could be determined several factors had to be established. First a suitable family of salts had to be selected. The next step involved determining that no part of the apparatus react with the salts in molten conditions. A methodology for determining reaction was selected by Dr. Flowers after trial by research students. The trials were based on ferrocene/naphthalene cooling curve plotting (see Figure 1). This process was refined to the point that it was used to determine the cryoscopic constant of the salts.

Cooling Curve Procedure

Reagents

Naphthalene C10H8, lot number 770233, Teflon tape, and lead (Pb), lot number 724460, were obtained from Fisher Scientific. Ferrocene $(C_5H_5)_4Fe$, lot number A16A, was obtained from Eastman Kodak Co. The ferrocene was additionally purified by allowing it to sublime to the tops of sealed test tubes.

Equipment used.

An Omega model 115 JC thermocouple digital thermometer was used to obtain temperature readings. A Barnsdedt Thermodyne type 4550 variable AC controller, Thermodyne Brisk-heat tape, an Omega Chrom alum-k type thermocouple and an Omega CN370 thermocouple controller were obtained from Fisher Scientific Co. (refer to figure 2). A Fisher Scientific strip chart recorder and a Lloyd Instruments

strip chart recorder were utilized as output devices. A Napco model 5831 vacuum oven and a Labcon Co., catalog #50002/3, glovebox were used in sample preparation.

A Digital Thermal Analyzer (DTA) was constructed using standard operational amplifiers and a 6 volt D.C. power supply. This operational amplifier circuit functions as follows (refer to Figure 4). Assume that an input signal, voltage in (which increases the DC amplifier output current), is applied across the input terminals from the (TC) thermocouple. The current output from the circuit flows through voltage drop resistor (R1) and the output impedance (Load) in parallel. Because R1 is several hundred times the size of R2, and because the current through R1 is smaller than the current through R2, it follows that the voltage across R1 will be many times the voltage across R2. This ratio is a measure of the amplification. Since the voltage across R2 is the input voltage, the ratio of R1/R2 represents the stage gain. The voltage amplifier is a high-gain, high-impedance circuit. After construction of the circuit it was found to have an unacceptable level of noise. This 0.4 volt noise level was found to be reduced by the insertion of a filter capacitor between the thermocouple and the differential analyzer circuit.

Procedure

Prior to constructing a proper experimental method, certain calibrations had to be performed. Since it was known

that a thermocouple output would be used, the thermocouples had to be calibrated. The process used for doing this was to take distilled H2O and cool it to 0 °C. The H2O was observed to supercool between -6 and -8 °C. Upon mechanical agitation, freezing was instantaneous and the thermocouple was calibrated to within 0.1 °C.

To begin methodology development a suitable solute had to be found and tested. Dr. Flowers suggested using ferrocene $(C_5H_5)_2Fe$ and naphthalene $C_{10}H_8$, ferrocene as the solute and naphthalene as the solvent. The mixture was first heated beyond the melting point and left for various amounts of time to allow for even distribution and melting point depression by the ferrocene. An apparatus was constructed using heating tape and thermocouples connected to a digital readout (Figure 2).

In an example of a typical naphthalene/ferrocene run, 2.77 grams of naphthalene was mixed with 0.129 grams of ferrocene to yield a 0.25 molal solution. The analog output of the thermocouples was plotted on an x-y-t plotter to determine freezing point depression. Since any content of soluble material within the naphthalene or salt will result in a depression of the freezing point(5), this process was deemed suitable to establish the cryoscopic constant. The depression of freezing point is related to the concentration of solutes dissolved according to the equation

$$T_f^{\circ} - T_f = K_f m$$

where T_f^o is the freezing point of the pure solvent, T_f is the freezing point of the solvent plus dissolved solute, K_f is the cryoscopic constant, and m is the molal concentration of solute.

During the development of this protocol, it was found that the cooling curves as shown in Figure 1 were difficult to interpret. It was decided at this point that the signal from the thermocouple would have to be amplified and differentiated so that the inflection point on the curve would be made readily apparent. The (DTA) was used to accomplish this (see Figure 5).

After the ferrocene\naphthalene trials were completed, the method of investigation was established as follows. Each salt would be dried and tested for proper melting point. They would then be exposed to elements of the materials used in the cell apparatus and then cooling curves would be plotted to look for anomalies.

Ammonium Salt Compatibility Procedure

Reagents

The reagents used for the compatibility portion were tetrapentylammonium bromide, Aldrich lot# LX0200EW and tetrapentylammonium bromide, Kodak lot# C10R,C102120. Teflon, Viton, Pb and CaF_2 were also used as elements in this stage.

Equipment used.

As with the previous experiment, the Omega model 115 JC

thermocouple digital thermometer was used to obtain temperature readings. A Barnsdedt Thermodyne type 4550 variable AC controller, Thermodyne Brisk-heat tape, an Omega Chrom alum-k type thermocouple and an Omega CN370 thermocouple controller were utilized as were the Fisher Scientific strip chart recorder and Lloyd Instruments strip chart recorder.(Figure 6) The Napco model 5831 vacuum oven and a Labcon Co., catalog #50002/3, glovebox were used in sample preparation and the Digital Thermal Analyzer (DTA) was used to convert the output to readable form (Figure 5).

Procedure

The decision to use a series of ammonium bromides was largely based on Dr. Flowers' experience with the low melting point of the salts and the commercial availability of the entire series from multiple sources. This avoided the need for preparation of these salts (via metathesis) as a part of the experimental procedure.

The first step in compatibility testing was the drying and sample preparation. This involved the removal of the salt from the manufacturers' container and melting the salt to drive off any extraneous water. The ammonium bromide series is known to be hygroscopic to the extent that it will deliquesce in normal atmosphere. This necessitated the use of glove bags under a constant nitrogen purge for all sample preparation. Within the glove bag the samples were weighed, and placed within a suitable container for slow drying. The

samples were then placed in a vacuum oven for a period of at least 24 hours. At this point they would be removed from the oven. Then the sample would be placed in the glove bags and partitioned into individual test tubes for melting point determination.

Once melting points were established and found to be within the manufacturers' published parameters, a cooling curve was taken to establish a base line for the particular salt. Once a baseline cooling curve for each was established, samples of each salt were placed in a test tube with a small amount of apparatus elements in each. These were then heated beyond the melting point of the salt and maintained at a temperature within 4 °C of the melting point for periods of 1 to 24 hours. In the 24 hour samples, minor freezing point depressions were observed. The depressions were investigated by use of a control and found to be caused by decomposition products within the salts.(4) An upper time limit for exposure to the apparatus elements was established at 8 hours. A table of results of the compatibility testing will be shown in Appendix B with the raw data shown in Appendix C.

Once the apparatus elements were found to be non-reactive with the sample salts, further experimental refinement was pursued. Through testing of the FTIR cell (see Figure 3), it was determined that the Viton and Teflon o-rings would not withstand the pressures needed to

establish a supercritical environment. It was determined that Pb gaskets would withstand the pressure. Compatibility testing had to be conducted with the salts and the Pb. It was found that the lead was also not reactive with the salt, and therefore, a suitable apparatus element.

Another refinement of the process included sealing the salts within a glass vacuum tube. This was done with an oxygen acetylene torch. Non-standard test tube sizes had to be manufactured to accommodate the proper sealing of the salt under vacuum conditions. These were constructed using glass tubing and the acetylene torch.

Determination of Cryoscopic Constants Procedure

Reagents

tetrapentylammonium bromide Kodak lot# C10R,C102120
tetrahexylammonium bromide Kodak lot# A16A,B16C
tetraheptylammonium bromide Kodak lot# 0130221266
tetrapentylammonium bromide Aldrich lot# LX0200EW
tetrahexylammonium bromide Aldrich lot# MW07512AW
tetraoctylammonium bromide Aldrich lot# MX14108MX
ferrocene $(C_5H_5)_2Fe$, lot number A16A

Equipment used.

As with the previous experiment the Omega model 115 JC thermocouple digital thermometer was used to obtain temperature readings. A Barnsdedt Thermodyne type 4550 variable AC controller, Thermodyne Brisk-heat tape, an Omega

Chrom alum-k type thermocouple and an Omega CN370 thermocouple controller were utilized as were the Fisher Scientific strip chart recorder and Lloyd Instruments strip chart recorder. Napco model 5831 vacuum oven and a Labcon Co., catalog #50002/3, glovebox were used in sample preparation and the Digital Thermal Analyzer (DTA) was used to convert the output to readable form.

Procedure

The experimental procedure used to determine the (K_f) cryoscopic constants of the individual salts was similar to the naphthalene process. To determine a cryoscopic constant of a given substance, exact molal solutions, formula weights, and freezing point depression information are needed. The ferrocene/naphthalene experiments demonstrated that ferrocene was a suitably nonreactive substance to use as a solute in a molten salts solution.

A typical (K_f) run consisted of removal of the salt from the dried and tested containers. Approximately 0.54 grams of tetrahexylammonium bromide would be placed inside a test tube under constant nitrogen purge. Added to this would be 0.0352 grams of ferrocene. This would yield a 0.648 molal sample solution. This would then be heated to a temperature of 105-107 °C. This was allowed to cool. During the cooling process the liquid would crystallize. During this change of phase the liquid would maintain a constant temperature through the crystallization leaving a characteristic

sigmoidal curve. The solution would then be re-heated to approximately 105 °C and the plotted again. This process was then repeated and additional six times. The curves were then evaluated and an average Melting/Freezing point established(6) (see figure 7). The samples were then returned to the glove bag and additional ferrocene was added. Then the new molal solution was melted and plotted.

During this portion of the experiment it was noted that for different runs of the a constant molal solution different melting points were observed. It was determined that the ferrocene was not diffusing properly throughout the solution and an additional step of agitation was needed to speed the even diffusion in the sample.

The cooling curves were then plotted through the operational amplifier circuit and the sigmoidal curve was translated into a differential peak (see Figure 4). The peaks allowed very accurate determination of the inflection point of the cooling curve function. Since the inflection point has to occur as the derivative changes sign (in this case goes from positive to negative) this also was the exact melting/freezing point. The following salts (K_f) were determined and compared with calculated estimates: tetrapentylammonium bromide, tetrahexylammonium bromide, tetraheptylammonium bromide and tetraoctylammonium bromide. Both the sigmoidal and differential curves can be seen in the appendices.

Results and recommendations

Once the cryoscopic constants for the salts had been determined there was enough information available to look into the use of the Fourier transform infrared spectrometer as a method of investigation. A process had to be determined that would yield a correlation between the cryoscopic constant and spectral features from the output of the FTIR. This correlation would yield partition equilibrium information and would be useful to determine the feasibility of using the salts as the mobile phase in an extraction process. The high pressure cell was constructed such that the denser molten salt would accumulate at the bottom of the cell and be available for spectral analysis. During this process it was found that solute diffusion rate problems occurred that were similar to the ones found in the cryoscopic determination procedure. The solution to this problem was similar to the solution in the previous procedure in that agitation facilitated the even distribution of solute to solvent. To achieve the agitation, the cell reflector was modified by placing a small magnet within it, and using a magnetic stirring device to mix the molten solution. The second portion of the experimental was designed to determine the equilibrium partitioning of various solutes between tetrapentylammonium bromide and CO_2. The cell preparation involved cleaning all the cell parts (see Figure 3) with a solution of isopropanol. The elements

were then dried in the vacuum oven overnight. The cell was then reconstructed inside the glove box under a constant nitrogen purge. Samples of tetrapentylammonium bromide prepared under vacuum seal were placed in the cell and sealed. The cell was then placed inside the FTIR and a background spectrum was taken. The cell was then heated above the melting point of the salt and pressurized to 800 psi. with CO_2. A sample spectrum was taken using 100 scans averaged and referenced to the background spectrum. This was accomplished digitally by the BioRad computer. Once a baseline spectrum had been determined, pressure variations were explored in an attempt to determine the solubility of CO_2 in tetrapentylammonium bromide. After this, samples of tetrapentylammonium bromide and other analytes were prepared to establish reactivity and possible partition equilibria for the analytes. The following analytes were tested: quinone, hydroquinone, phenol, benzoic acid and biphenyl ketone.

References

(1) Flowers, P.F., ACS-PRF Grant proposal, **1990**.

(2) Gordon, J.E. J. Amer. Chem. Soc. **1965**, 87(19), 4347-4358.

(3) Coker, T.G.; Ambrose, J.; Janz, G.J. J. Amer. Chem. Soc. **1970**, 92(18), 5293-5297.

(4) Gordon, J.E. J. Org. Chem. **1965** 30( ), 2760-2763.

(5) Skoog, D.A. "Principals of Instrumental Analysis", 3rd ed.; Saunders College Publishing: New York, **1985**, p. 47.

(6) Brady, J. E.; Holum, J. R. "Fundamentals of Chemistry", 3rd ed.; Wiley and Sons, Inc.: New York, 1988; p. 531.

Acknowledgements

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Figures 1-7

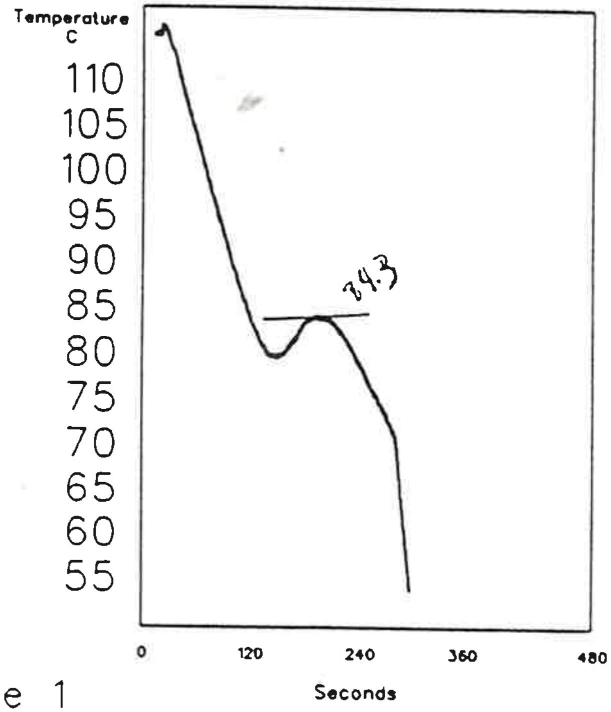

Typical Cooling Curve

Figure 1

Cryoscopic Equipment

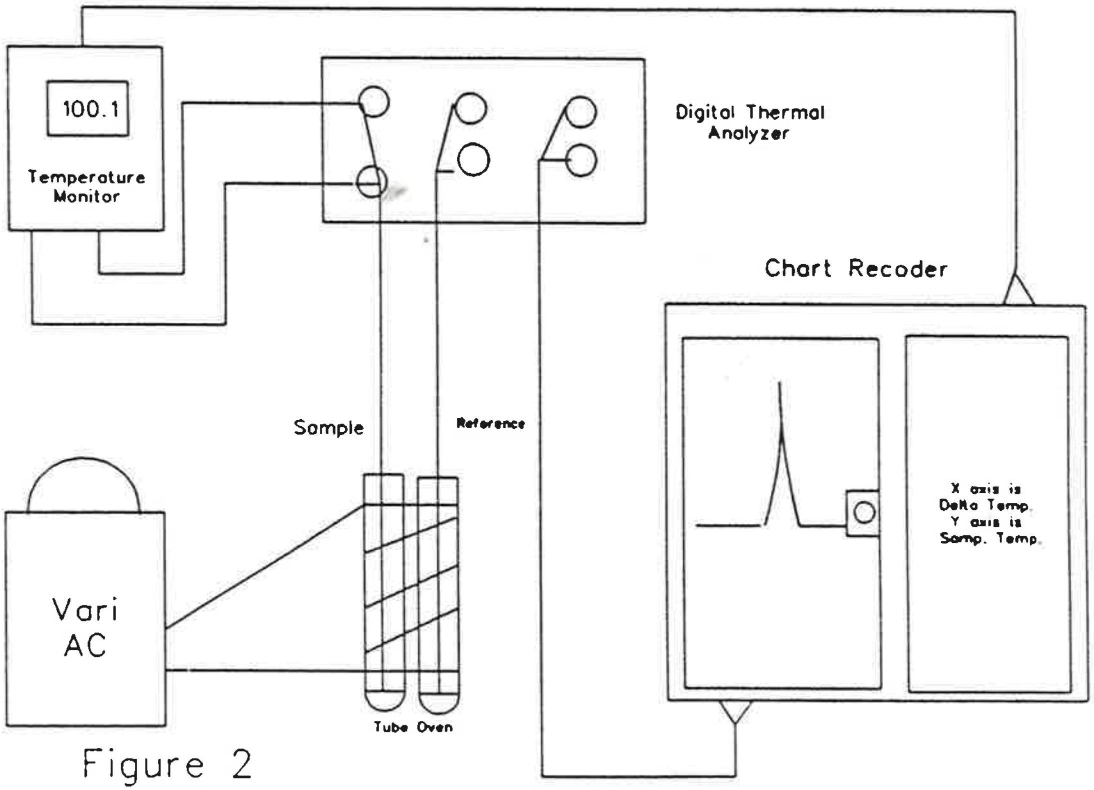


Figure 2

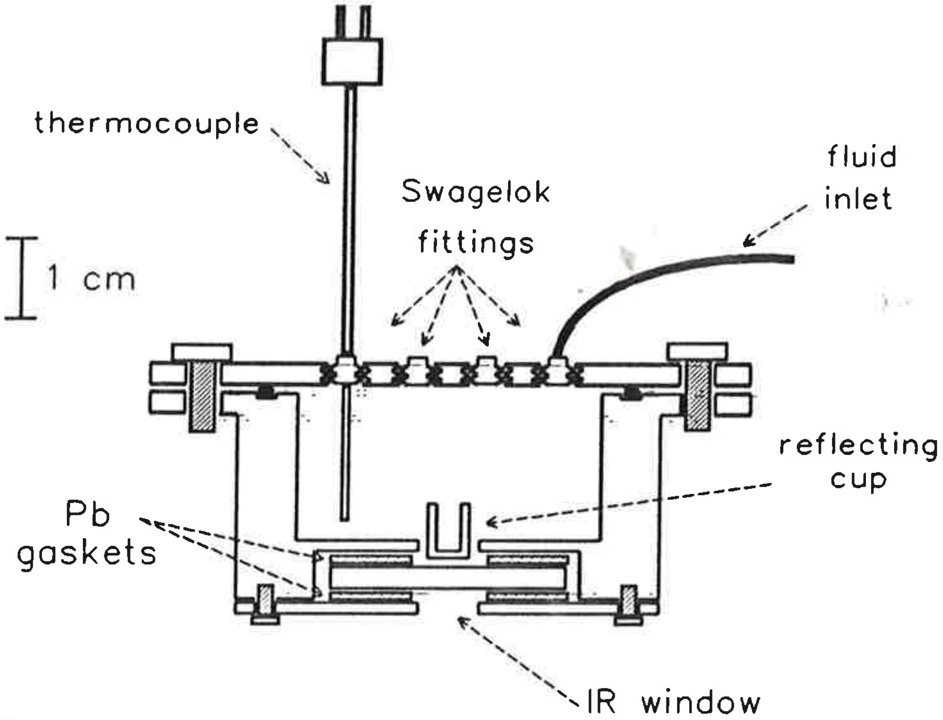
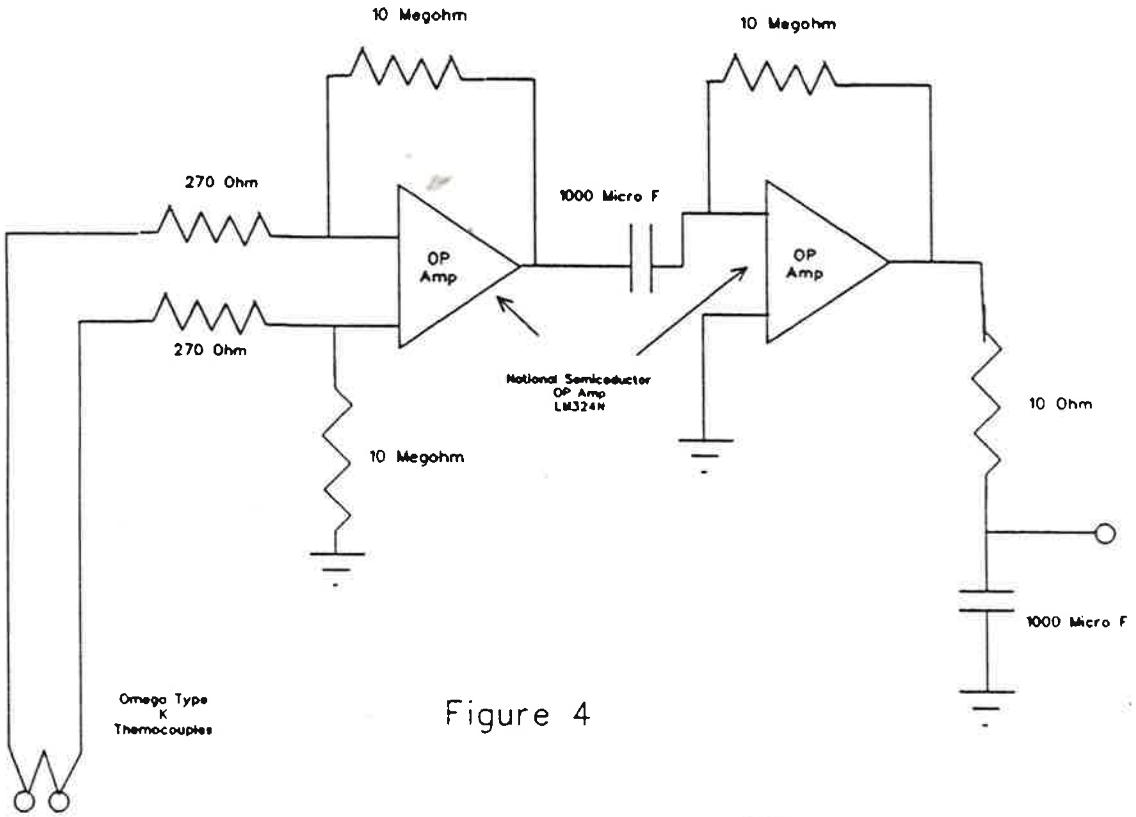

thermocouple
Swagelok
fittings
fluid
inlet
1 cm
reflecting
cup
Pb
gaskets
IR window

FIGURE 3

Digital Thermal Analyzer
Componant Schematic



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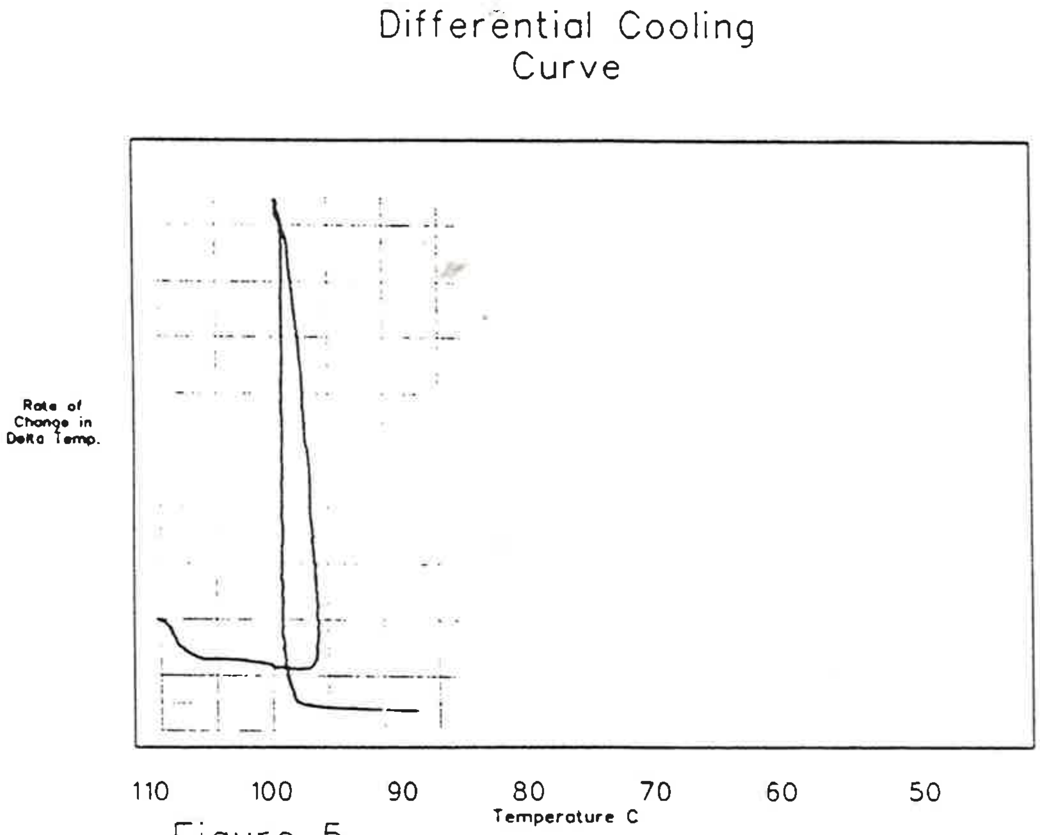
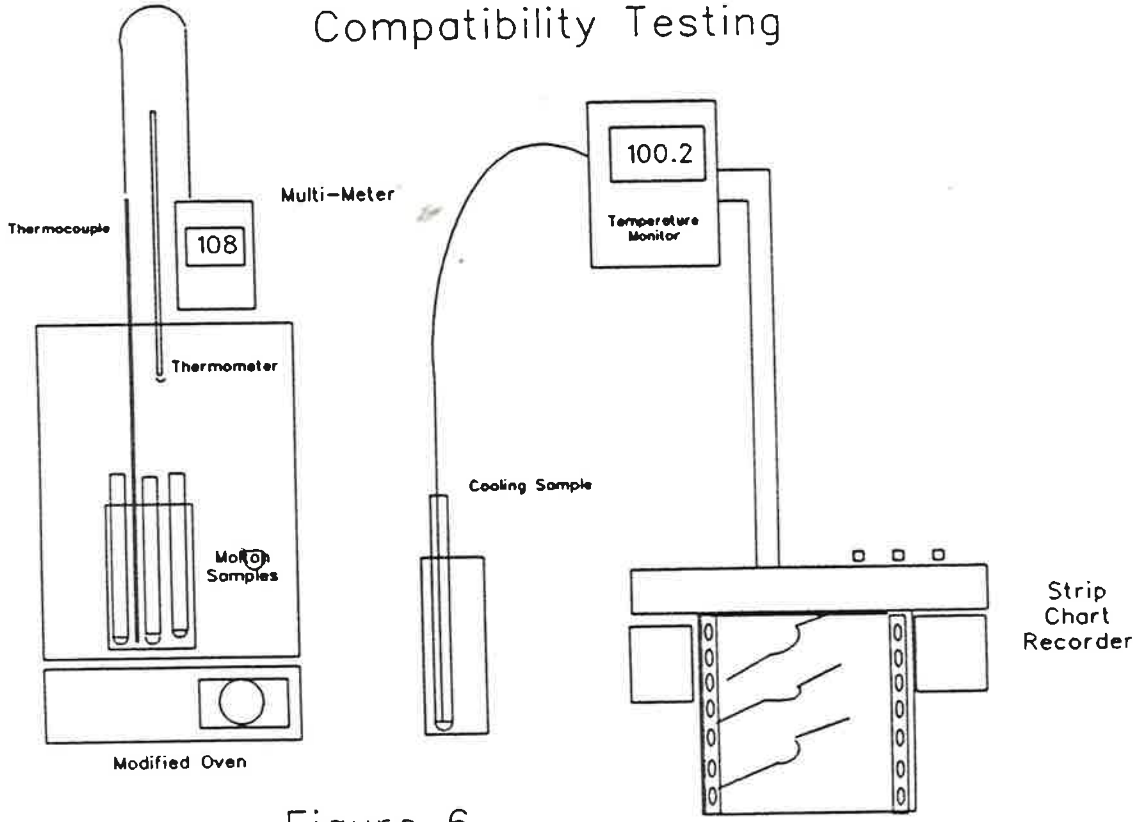

Differential Cooling
Curve
Rate of
Change in
Delta Temp.
110
100
90
80
70
60
50
Temperature C

Figure 5



Compatibility Testing

Figure 6

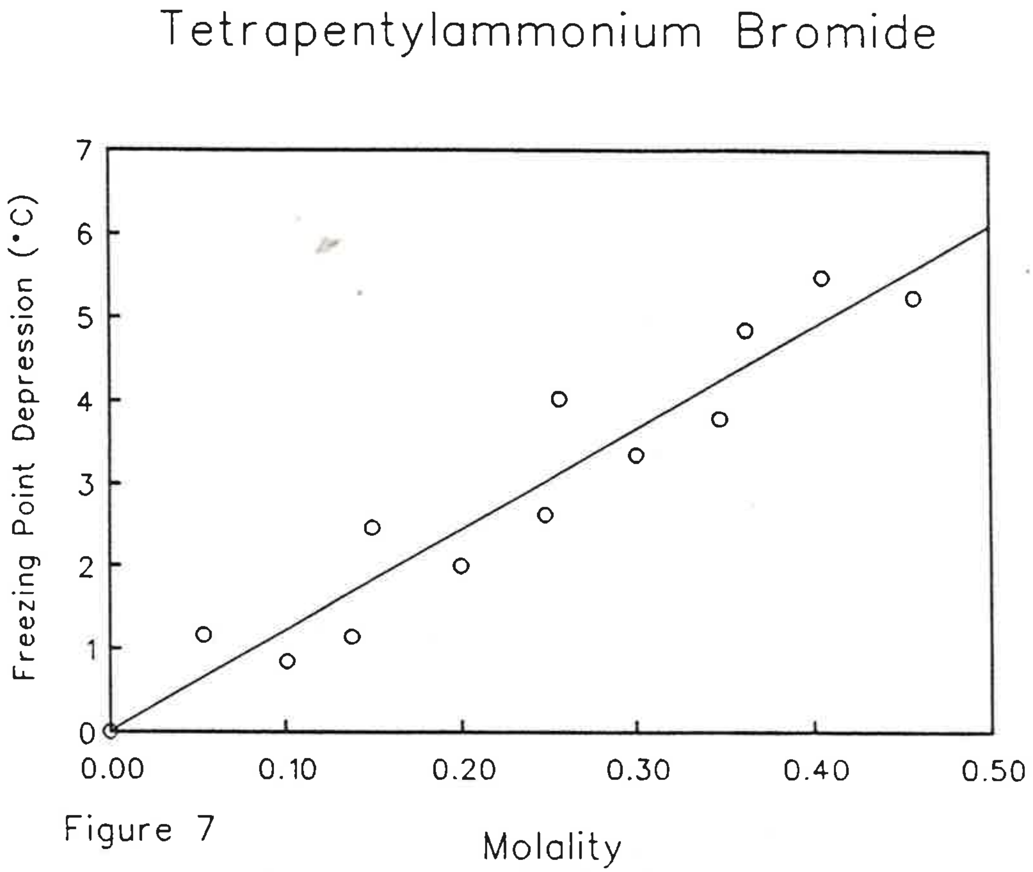

Tetrapentylammonium Bromide
Freezing Point Depression (•C)
0
1
2
3
4
5
6
7
0.00
0.10
0.20
0.30
0.40
0.50
Molality

Figure 7

Appendix A

Equipment and Reagent list

Biorad CPC3200 FTIR running Idris software

Omega model 115 JC thermocouple digital thermometer

Barnsdedt Thermodyne type 4550 variable AC controller

Thermodyne Brisk-heat tape

Omega Chrom alum-k type thermocouple

ISCO model 260D high pressure syringe pump

Omega CN370 thermocouple controller

Fisher scientific strip chart recorder

Loyd Instruments strip chart recorder

Napco model 5831 vacuum oven

Labcon Co. catalog #50002/3 glovebox

Tetrapentylammonium bromide Kodak lot# C10R,C102120

Tetrahexylammonium bromide Kodak lot# A16A,B16C

Tetraheptylammonium bromide Kodak lot# 0130221266

Tetrapentylammonium bromide Aldreich lot# LX0200EW

Tetrahexylammonium bromide Aldreich lot# MW07512AW

Tetraoctylammonium bromide Aldreich lot# MX14108MX

Appendix B

Compatibility testing results
for tetrapentylammonium bromide

Hours of Exposures

	0	.5	1.5	.5	8.0
A	97.4	99	97.4	93.0	94.6
B	97.9	98.1	98.0	97.0	95.4
C	99.9	98.5	98.9	97.2	97.4
D	98.9	99.4	98.7	97.0	97.0
E	95.4	94.2	97.8	96.0	96.5

Freezing/Melting temp. C

The sample legend is as follows;

A-control

B-Teflon O-ring Material

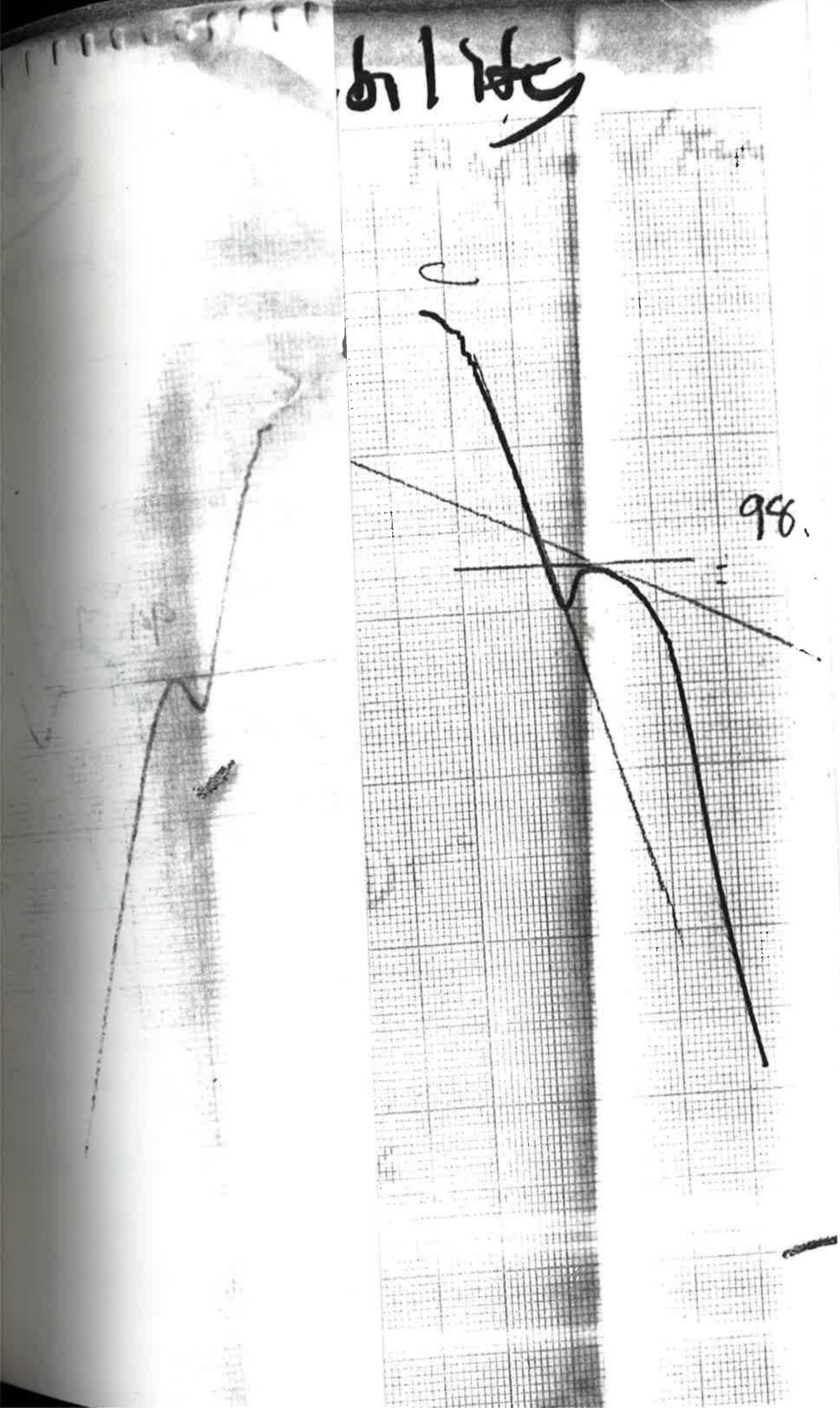
C-Pb (lead) Gasket material

D-CaF2 (Calcium Fluoride) Infrared window material

E-Viton O-ring material

The above table shows that the materials for the high pressure cell did not react with the salts and therefore were eliminated as a variable in the subsequent work.

Appendix C Raw Data


Sep 14
C
98.

7-5-AB compatibility

127.1

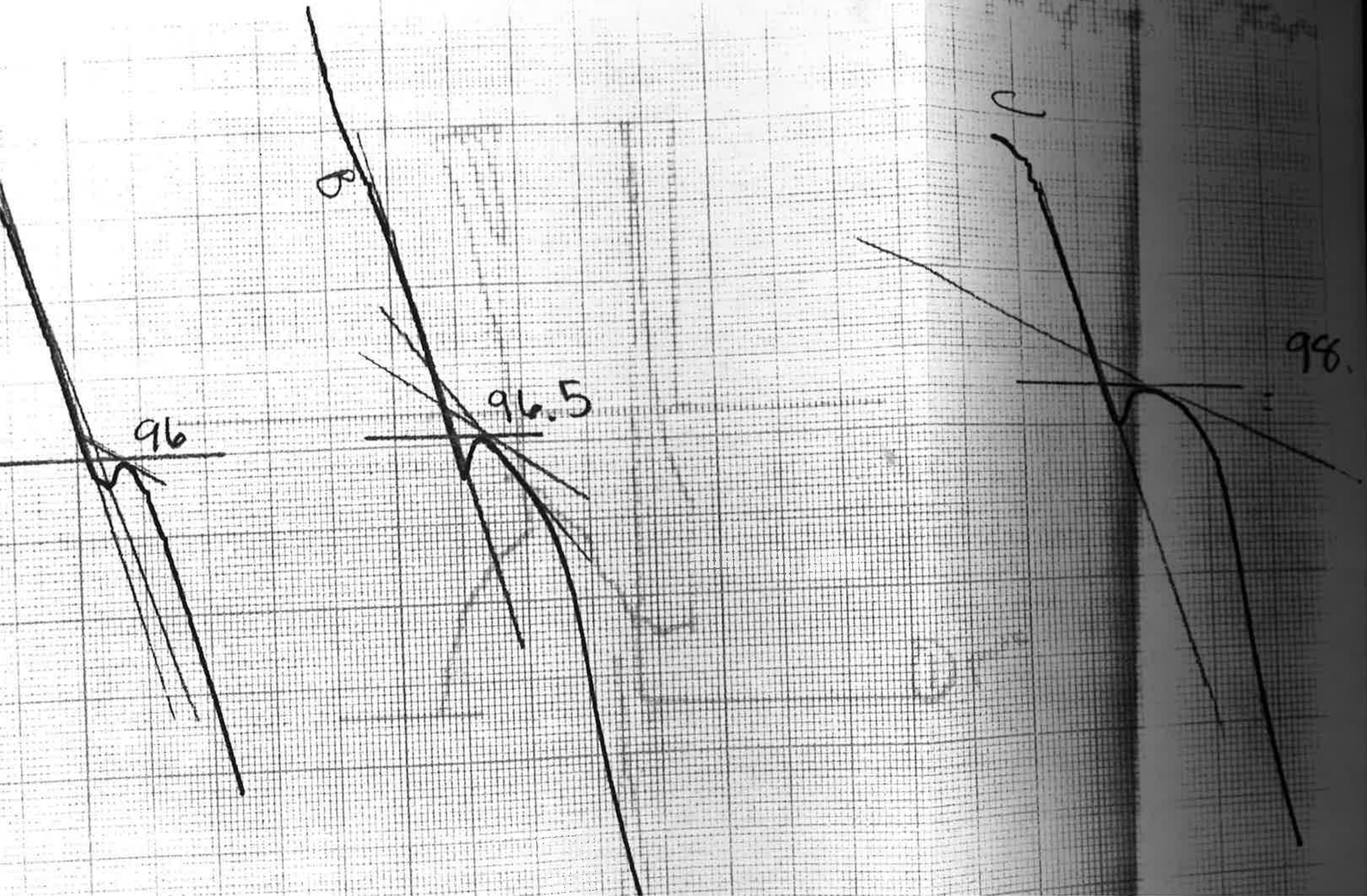
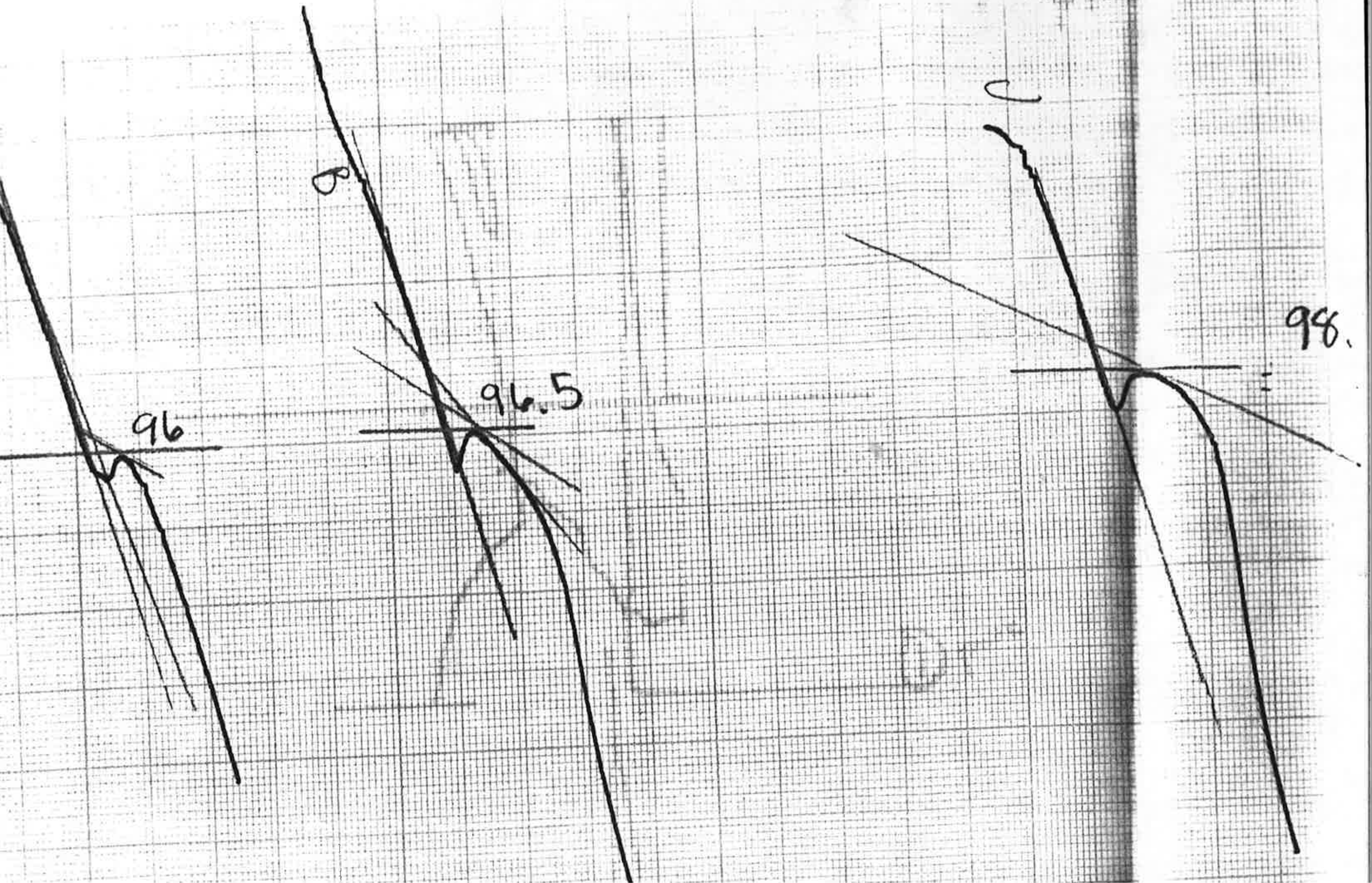


CHART No. CPP/0023/00

7-5-AB compatibility

127.1



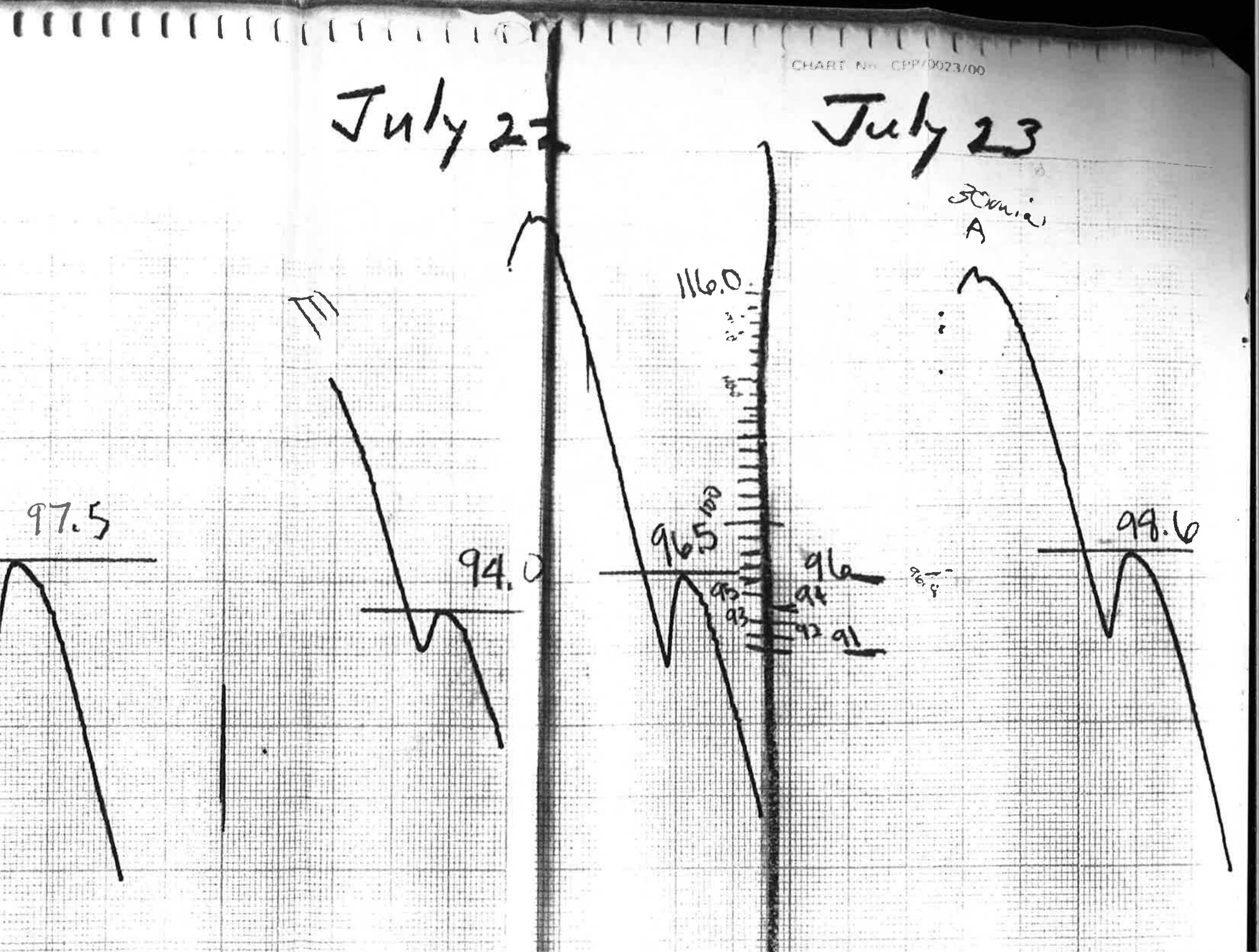
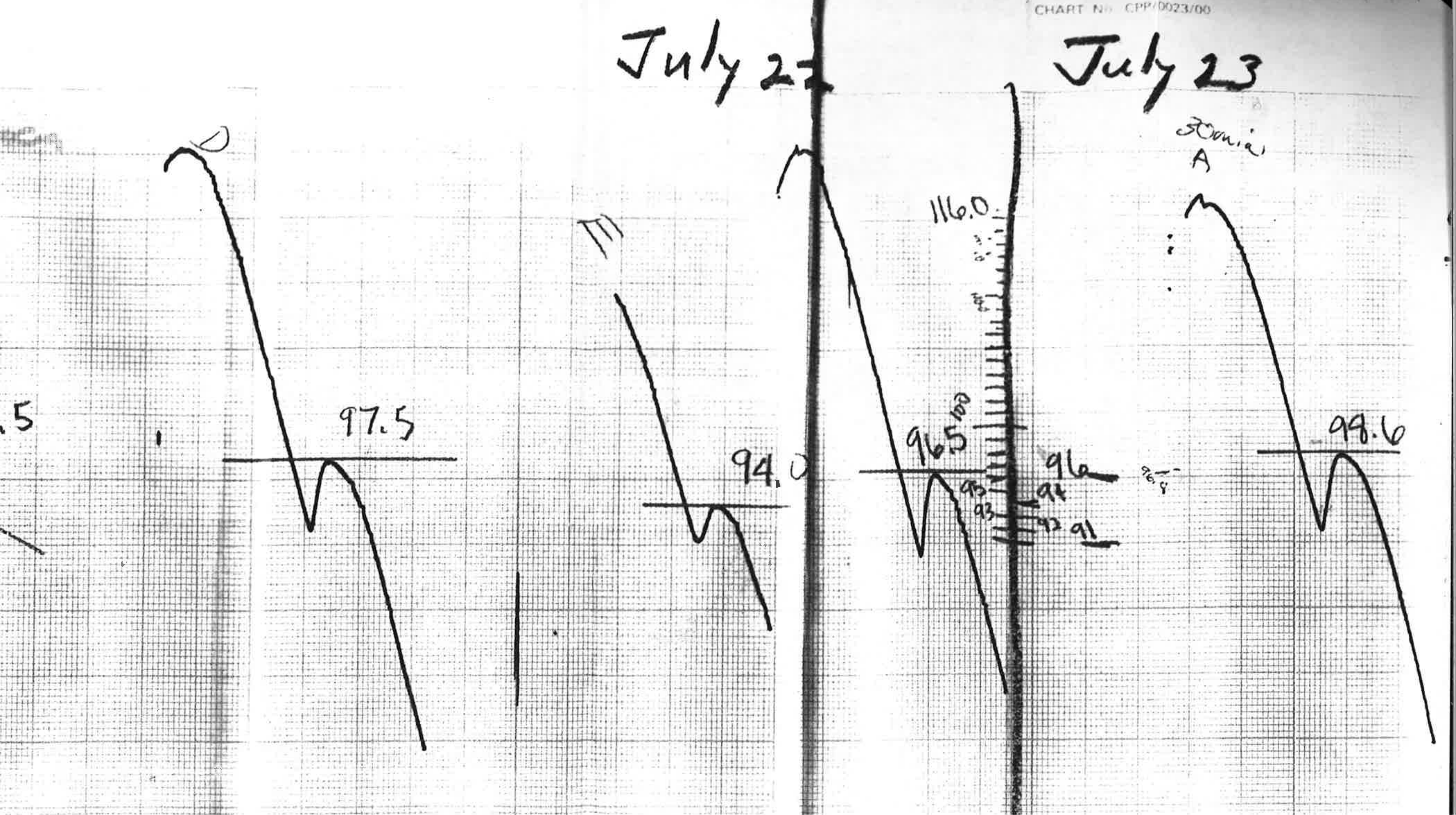


CHART No. CPP/0023/00
July 22
July 23
III
A
116.0
97.5
94.0
96.5
100
95
93
96
94
92
91
96.8
98.6

CHART No CPP/0023/00
July 22
July 23
.5
D
97.5
III
94.0
116.0
100
96.5
95
93
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92
91
30min
A
96.8
98.6

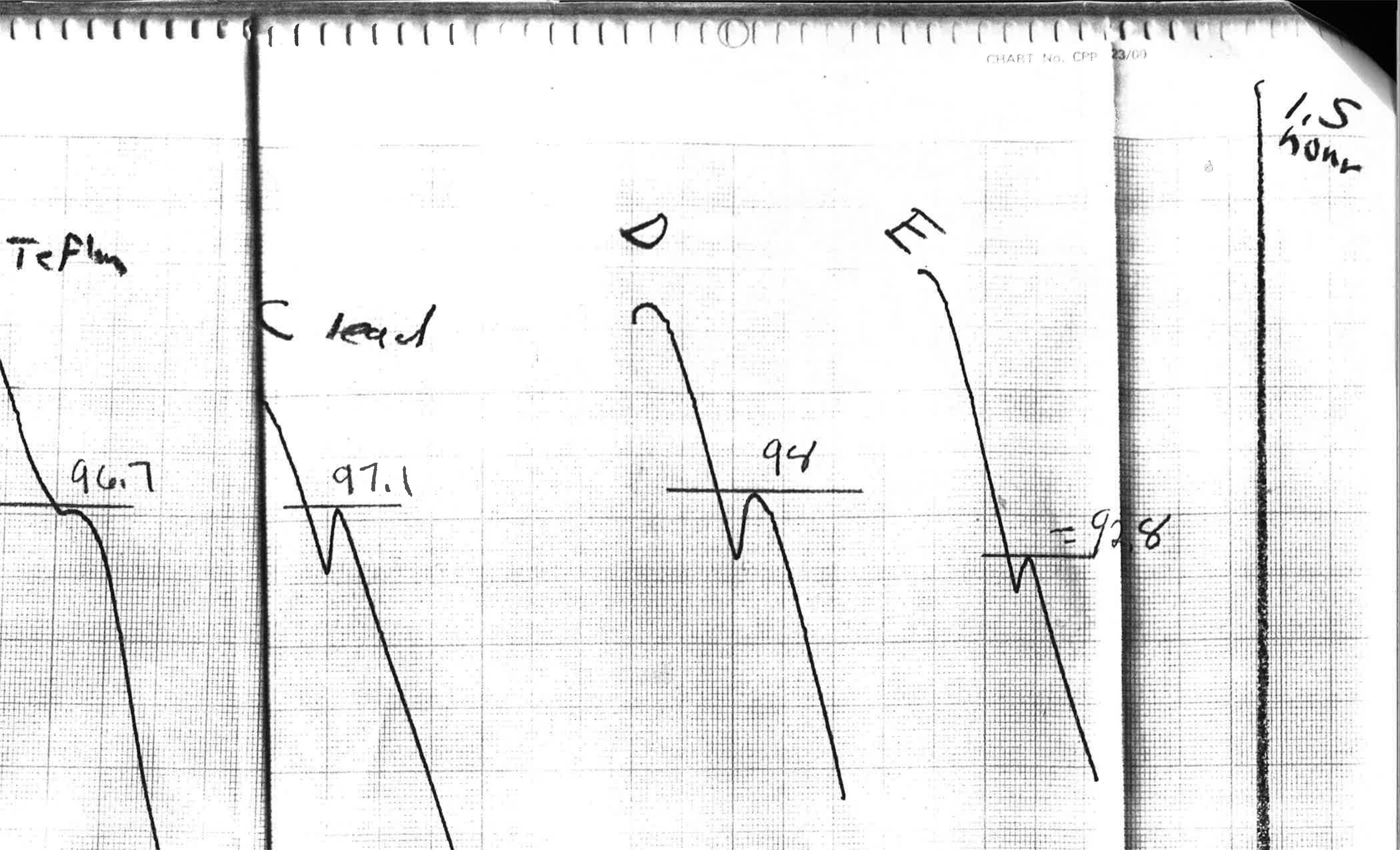
CHART No. CPP 23/00
Teflon
96.7
C lead
97.1
D
94
E
=92.8
1.5 hour

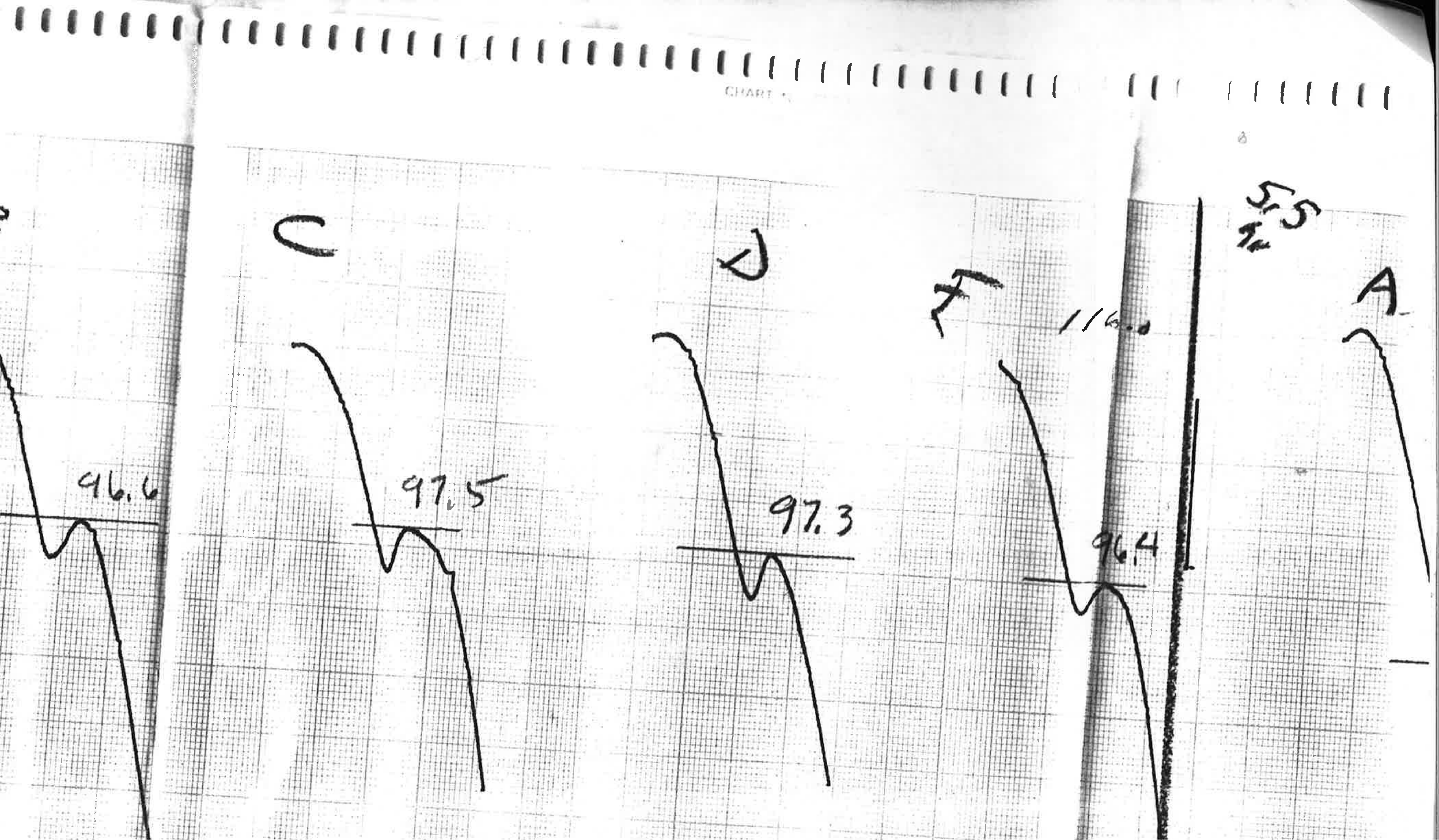
CHART
C
D
F
55
A
116.0
96.6
97.5
97.3
96.4

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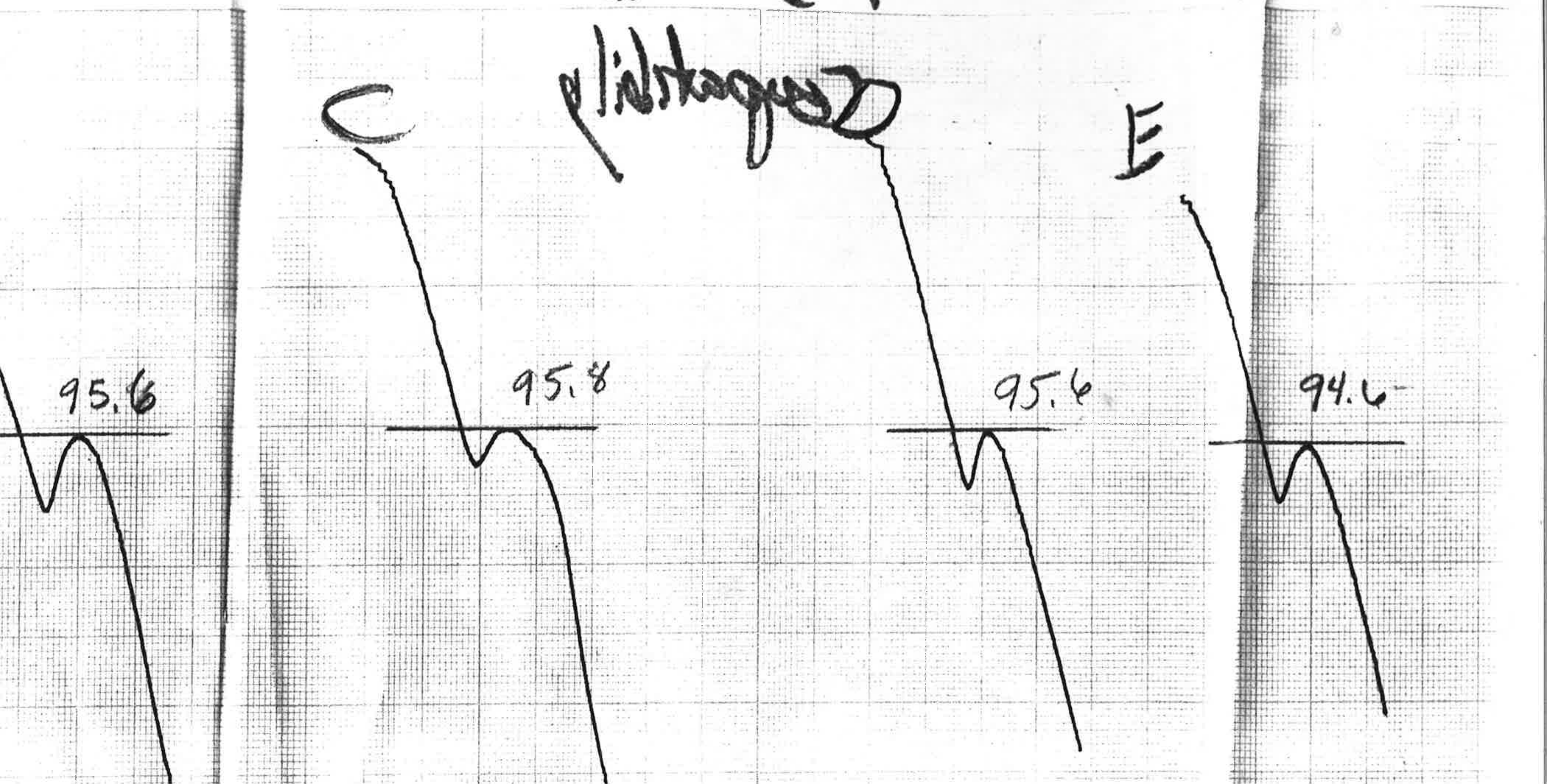
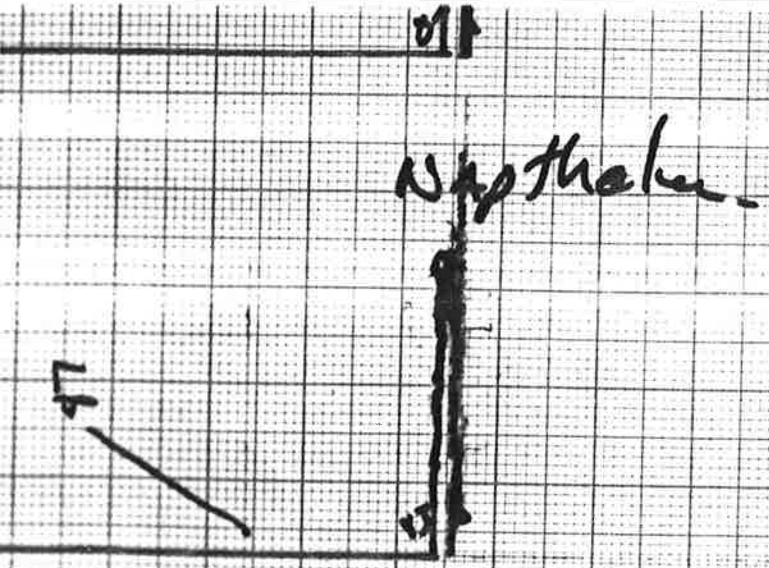
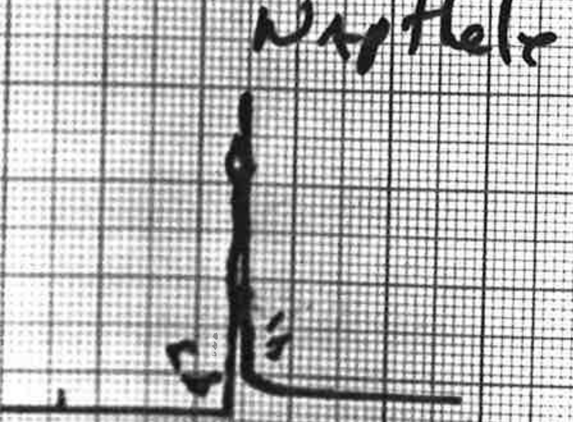



Napthalen-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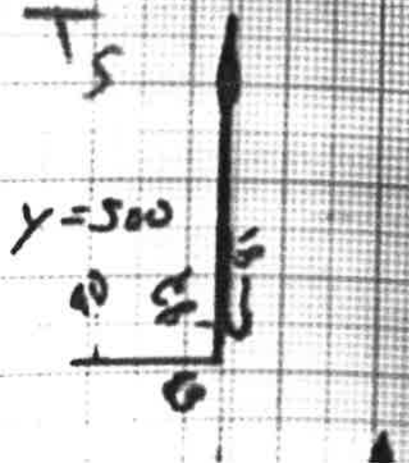
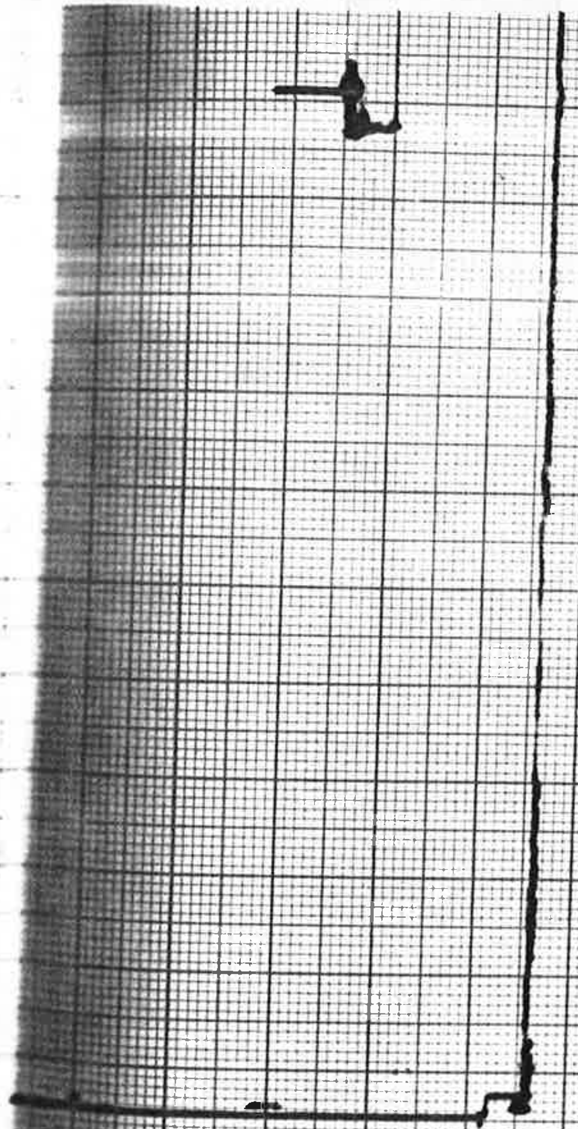
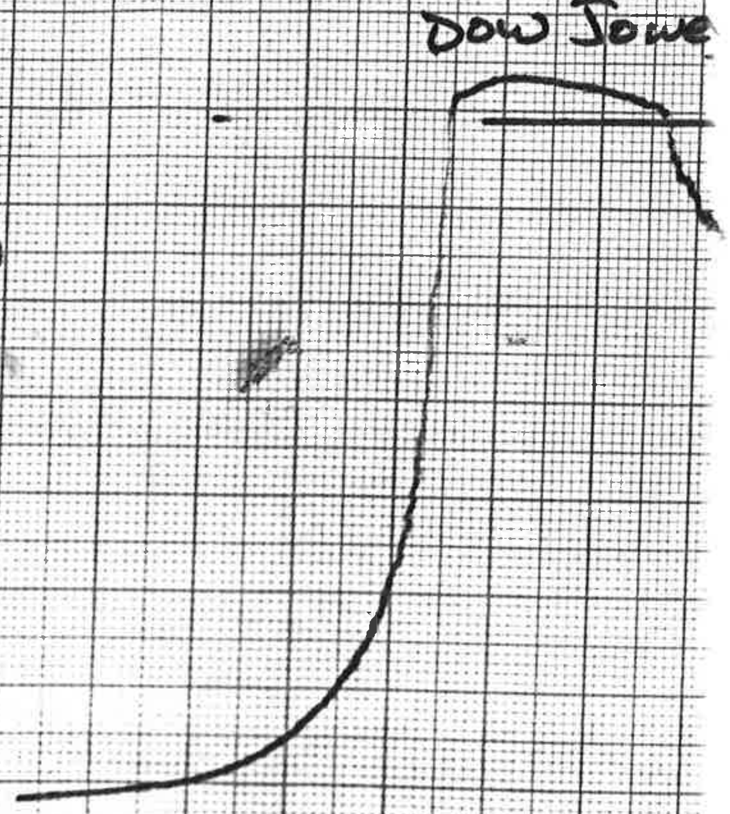
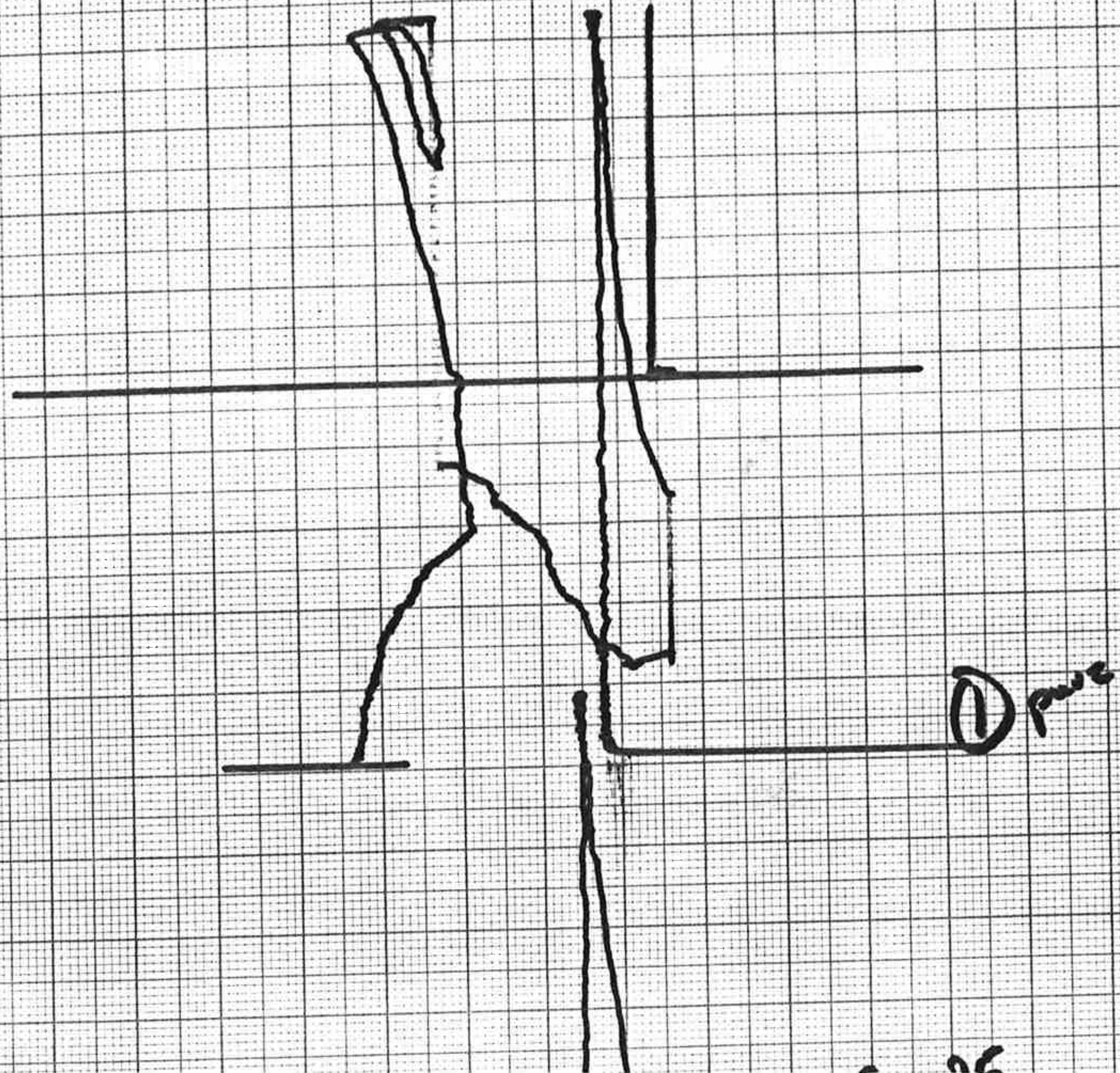

Ts
y=500
10
6




Dow Jone

Napthaly/Feroca



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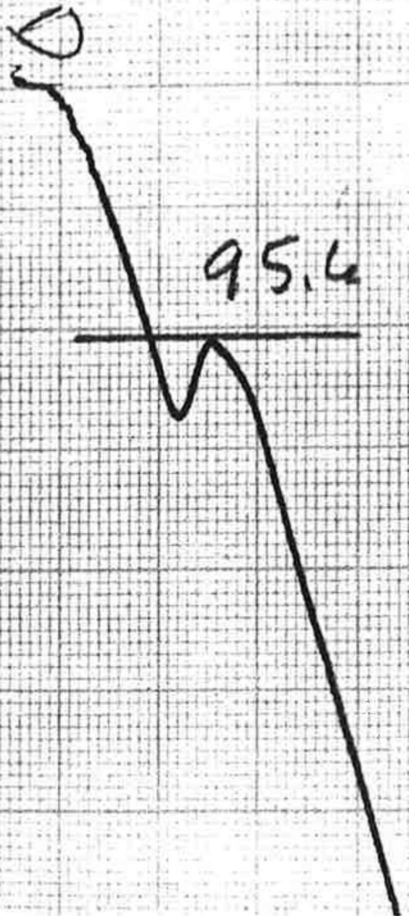
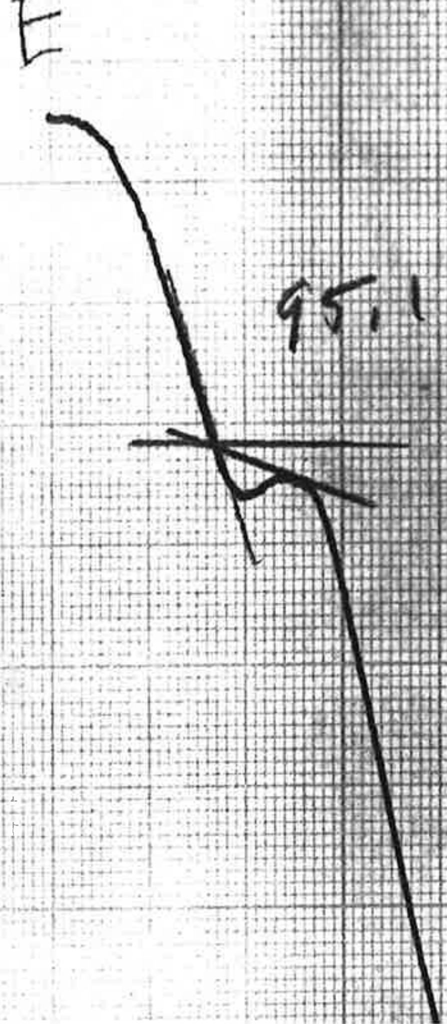




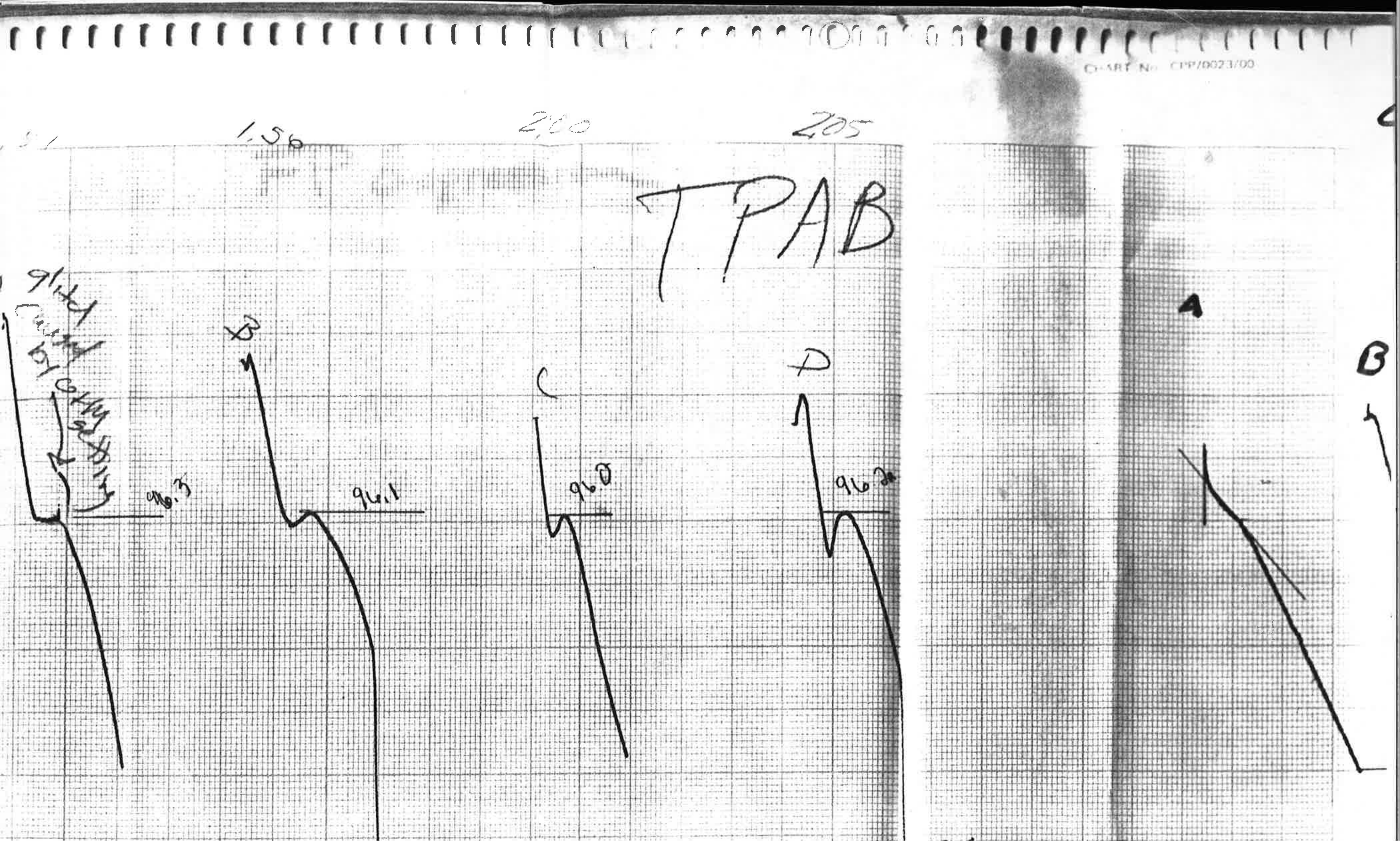
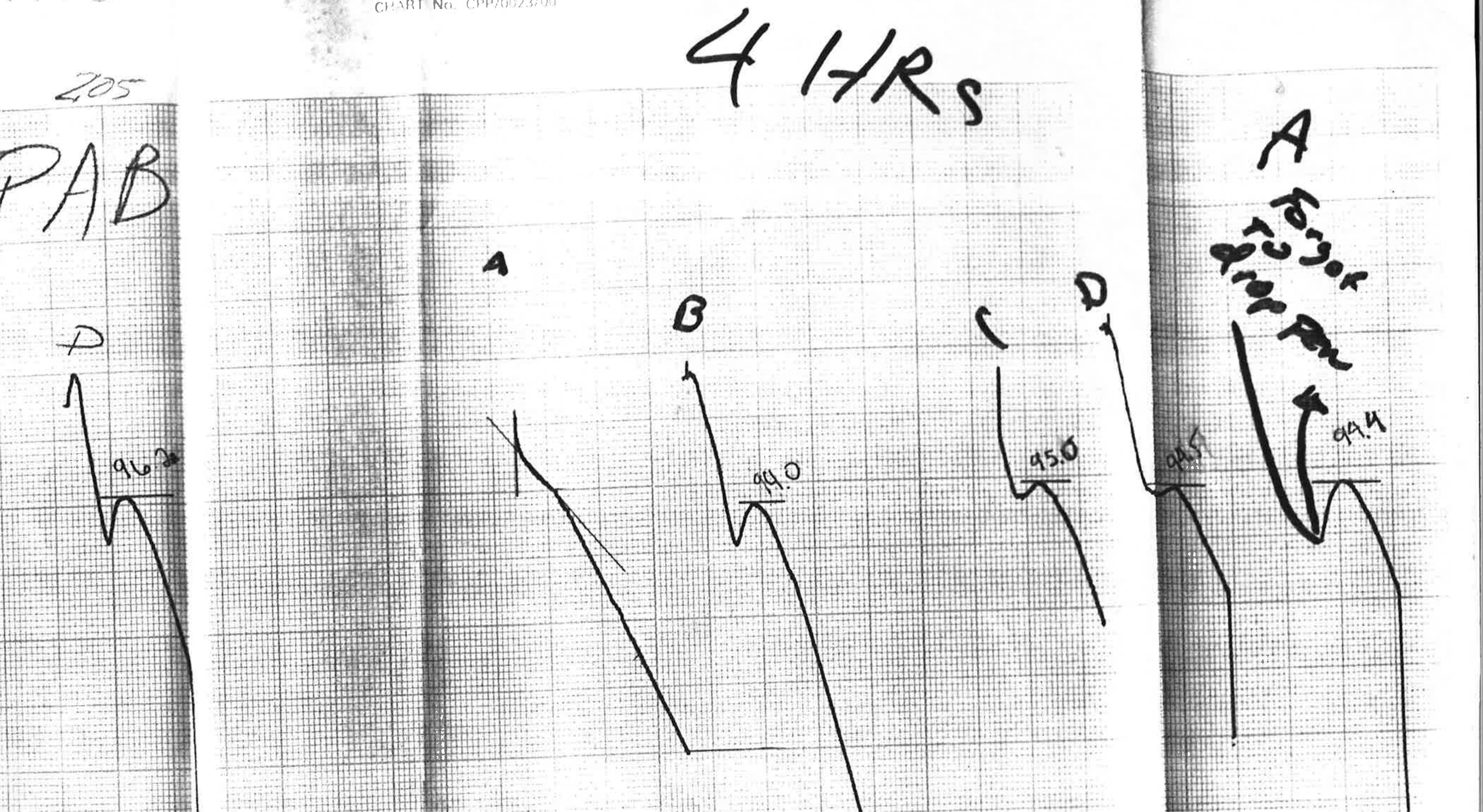


CHART No. CPP/0023/00
1:56
2:00
2:05
TPAB
9/14/01
Caused by
96.3
B
96.1
C
96.0
D
96.2
A
B

CHART No. CPP/0023/00



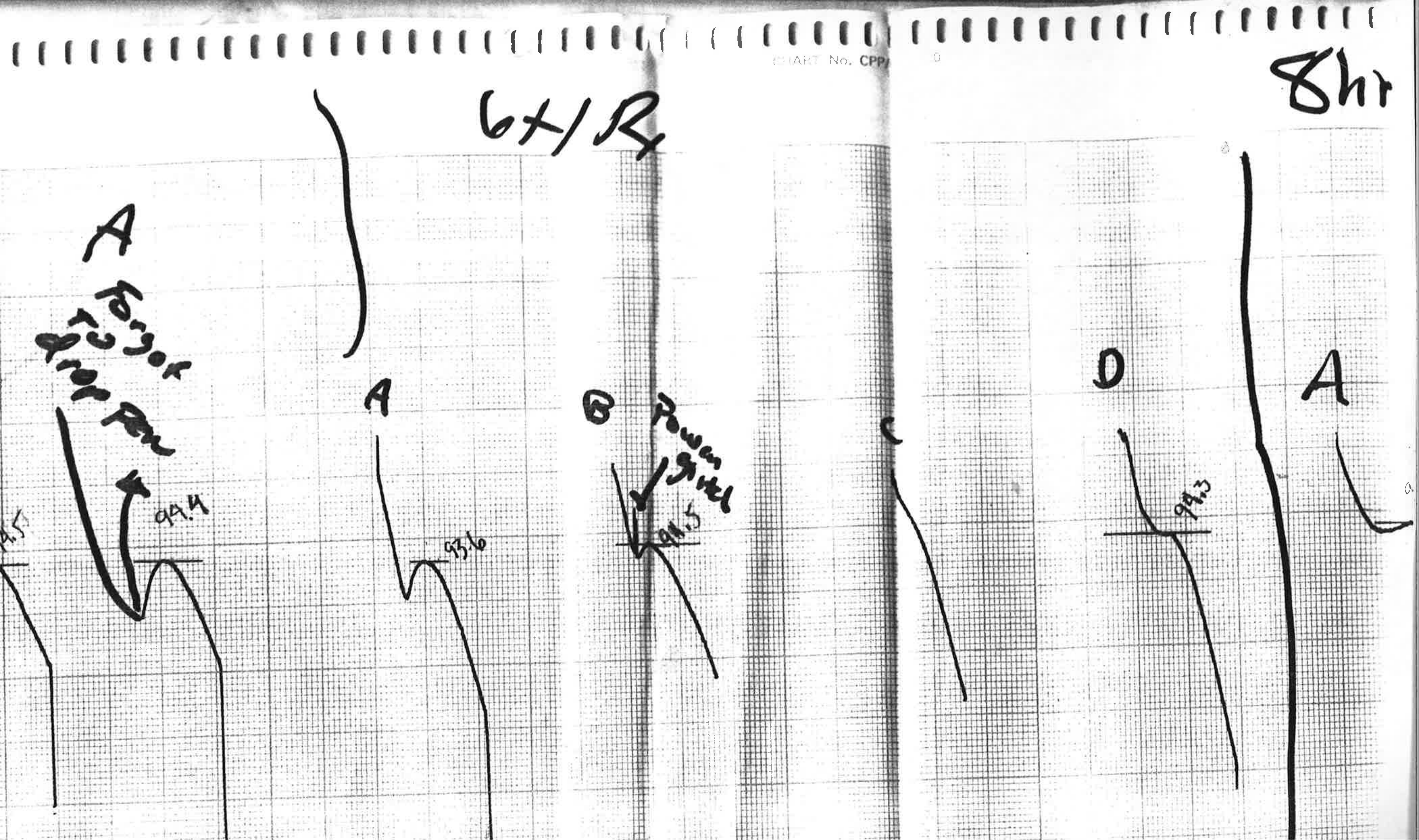


CHART No. CPP/
8hr
6x/Rx
A
A forgot to drop pen
9.5
99.4
A
93.6
B
Power glitch
99.5
C
D
99.3
A

CHART No. CPP/0623/00

10 hr

…rain
…with
…l agard
glass
…s & — Freezing
with
Tc moved
To center

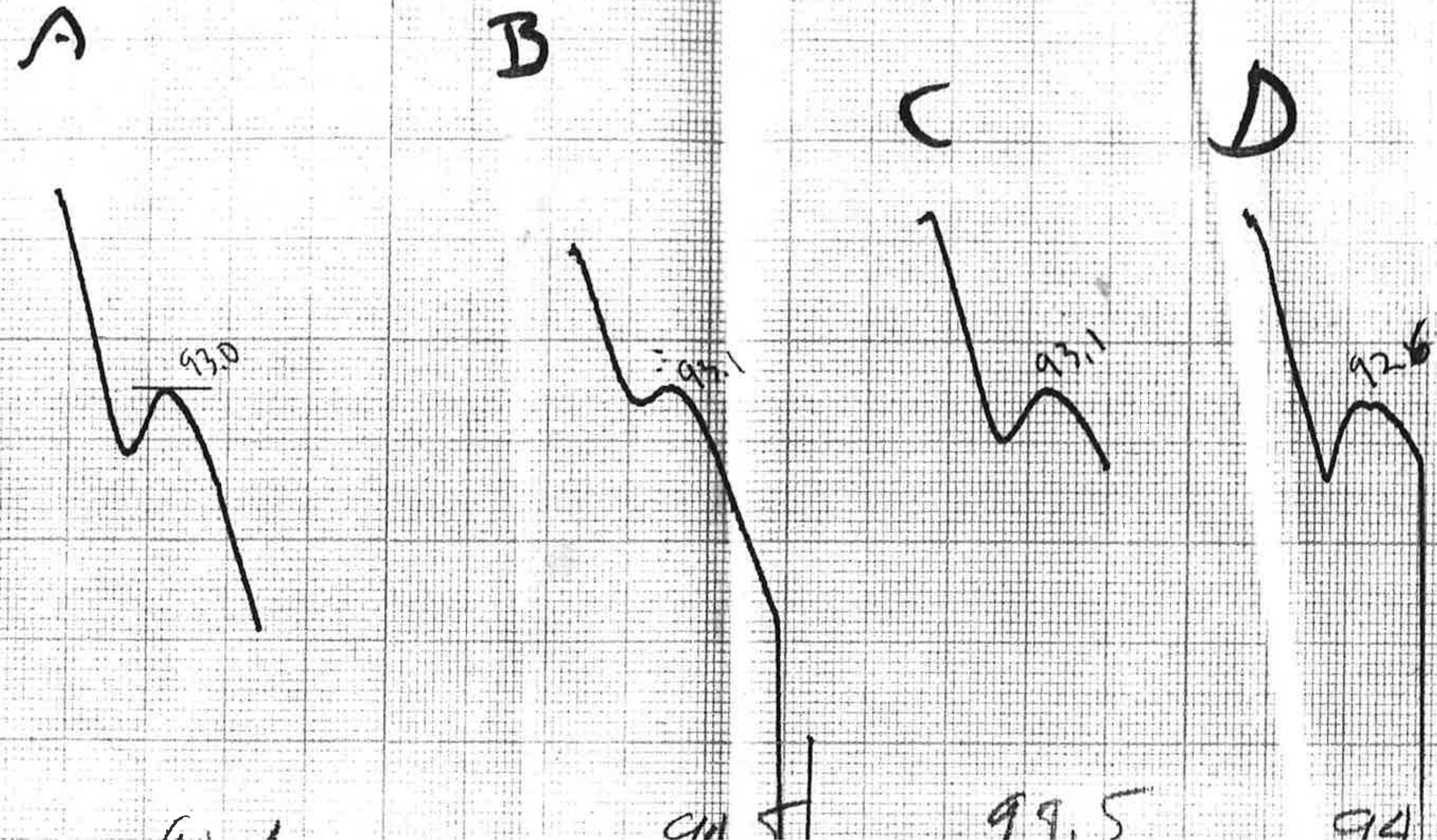
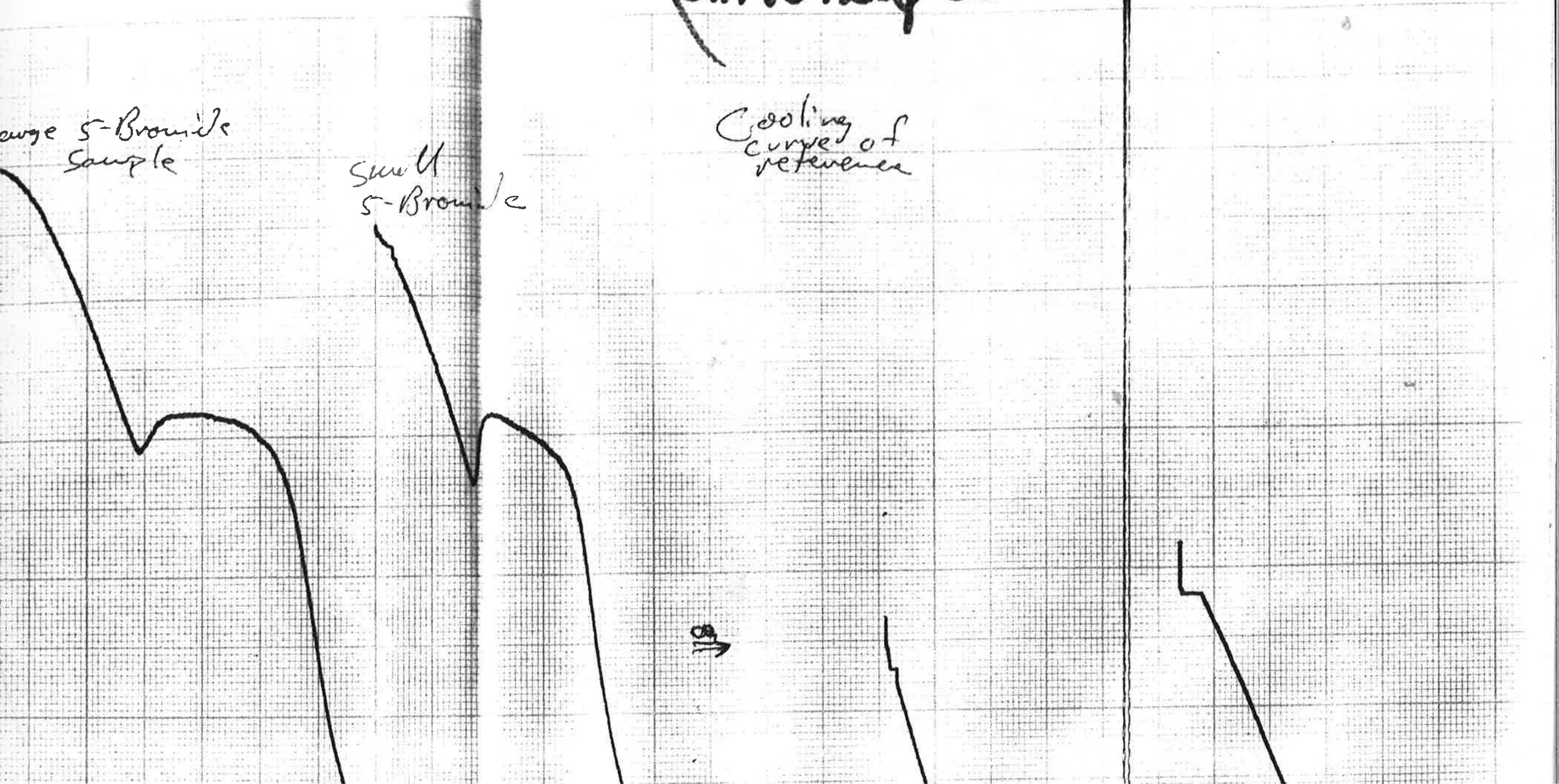
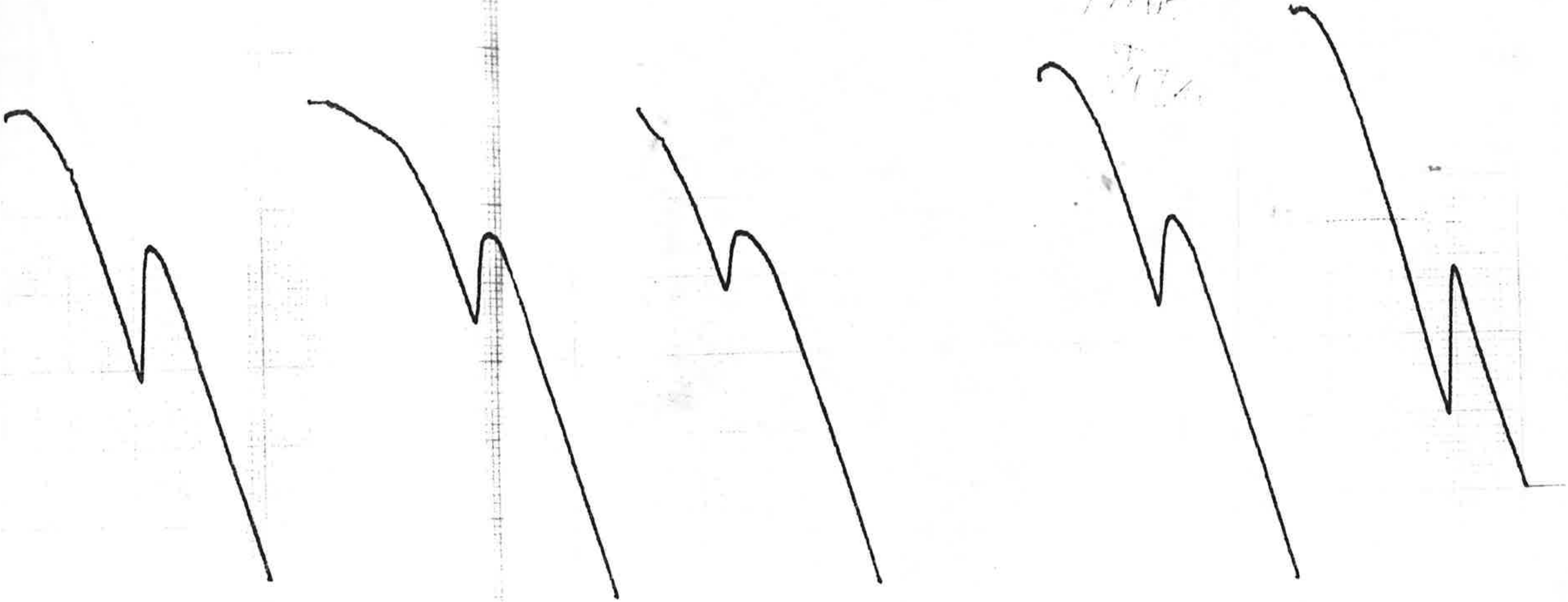
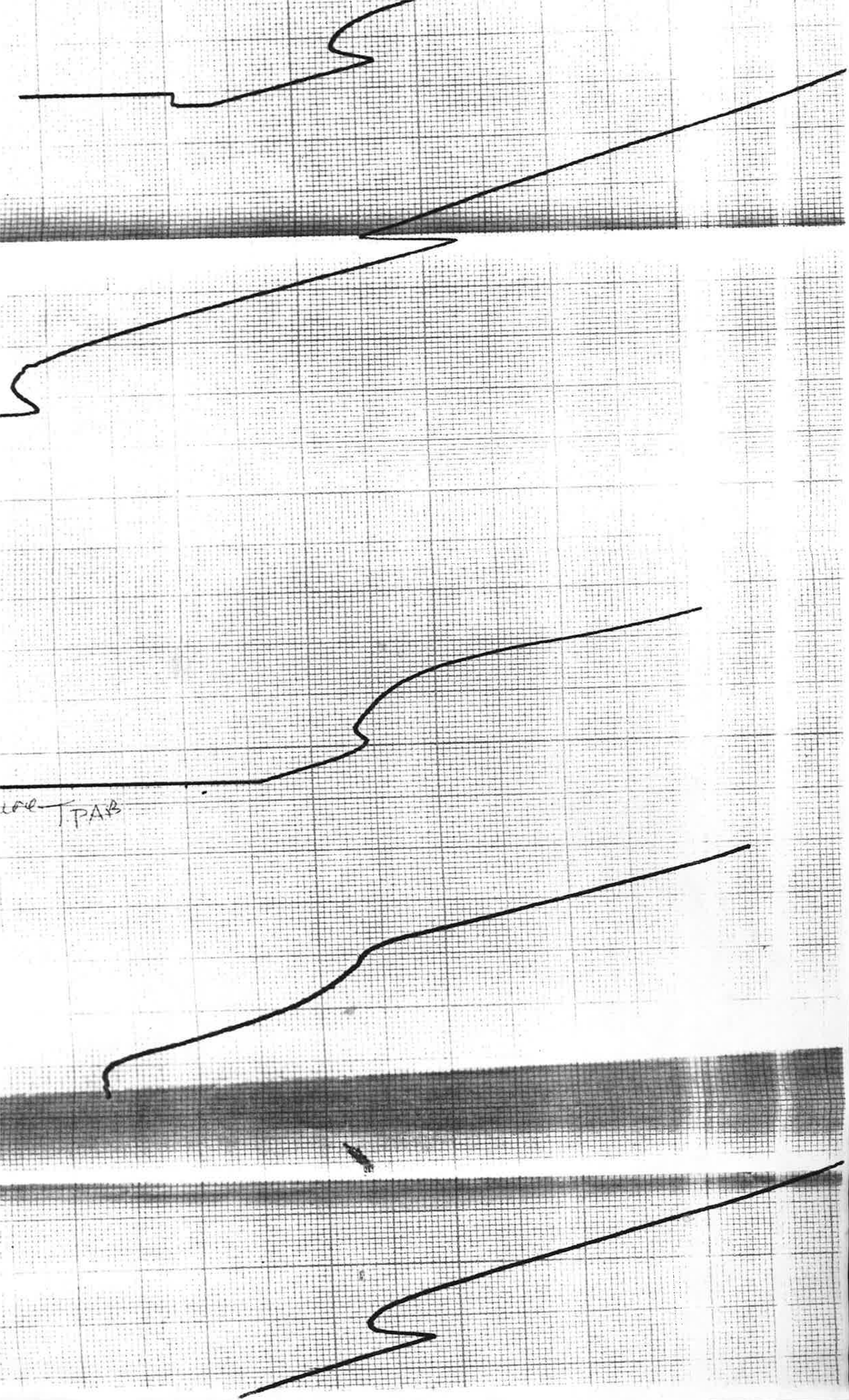


CHART No GPP/0623/00






PAB

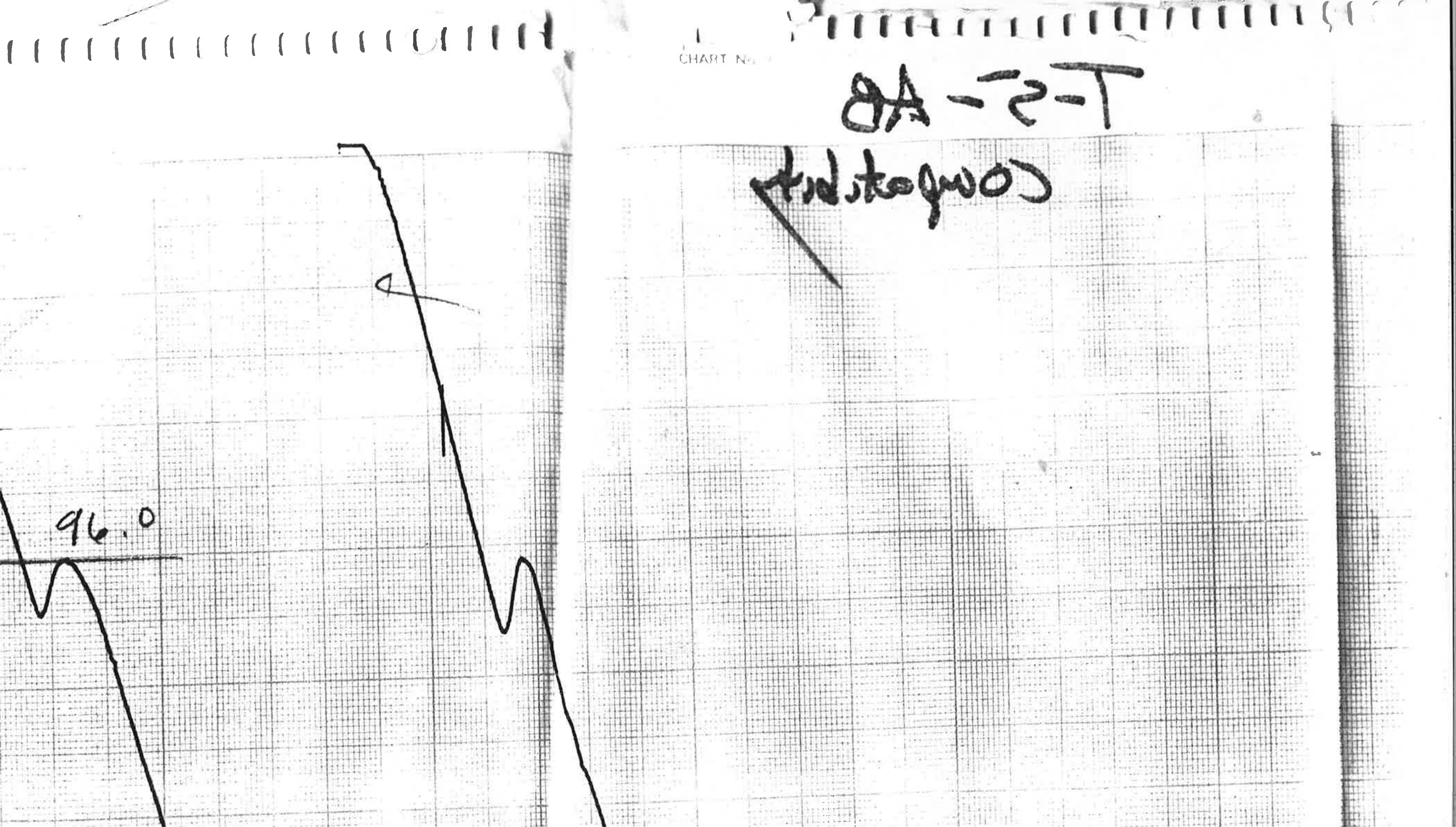


CHART N
96.0

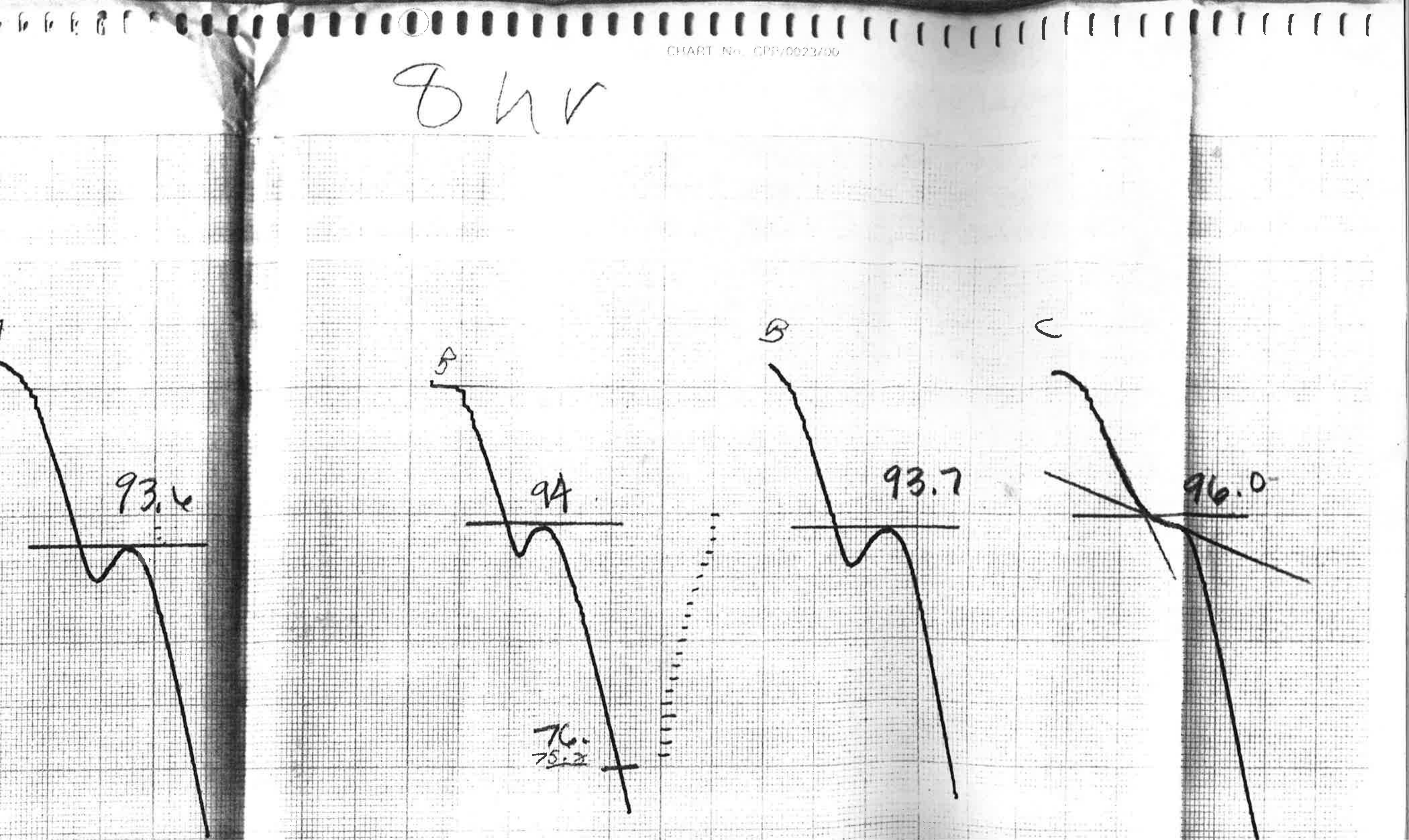


CHART No. CPP/0023/00
8hr
93.6
5
94
76.
75.2
5
93.7
C
96.0

CHART No. CPP/0023/00

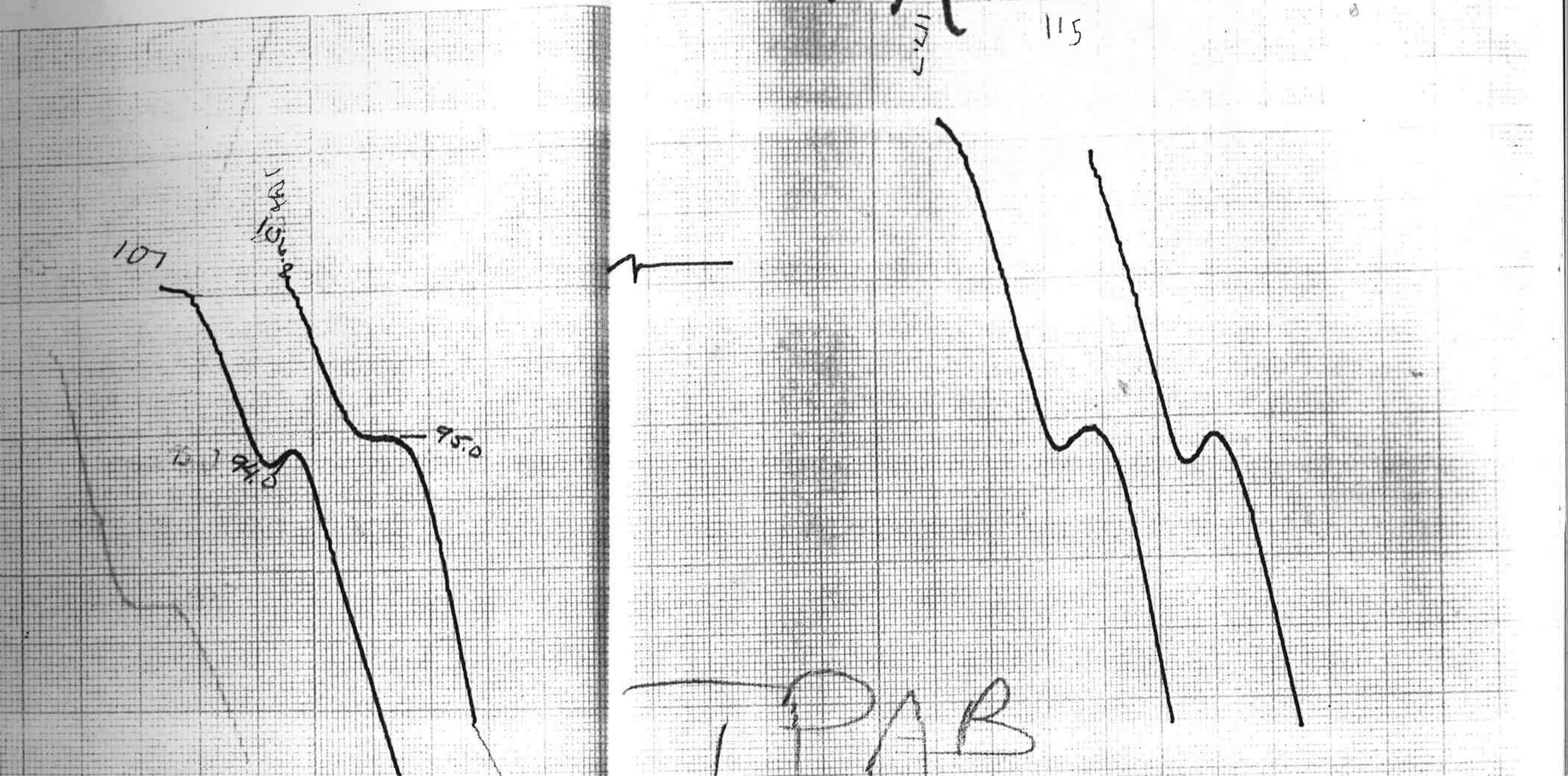
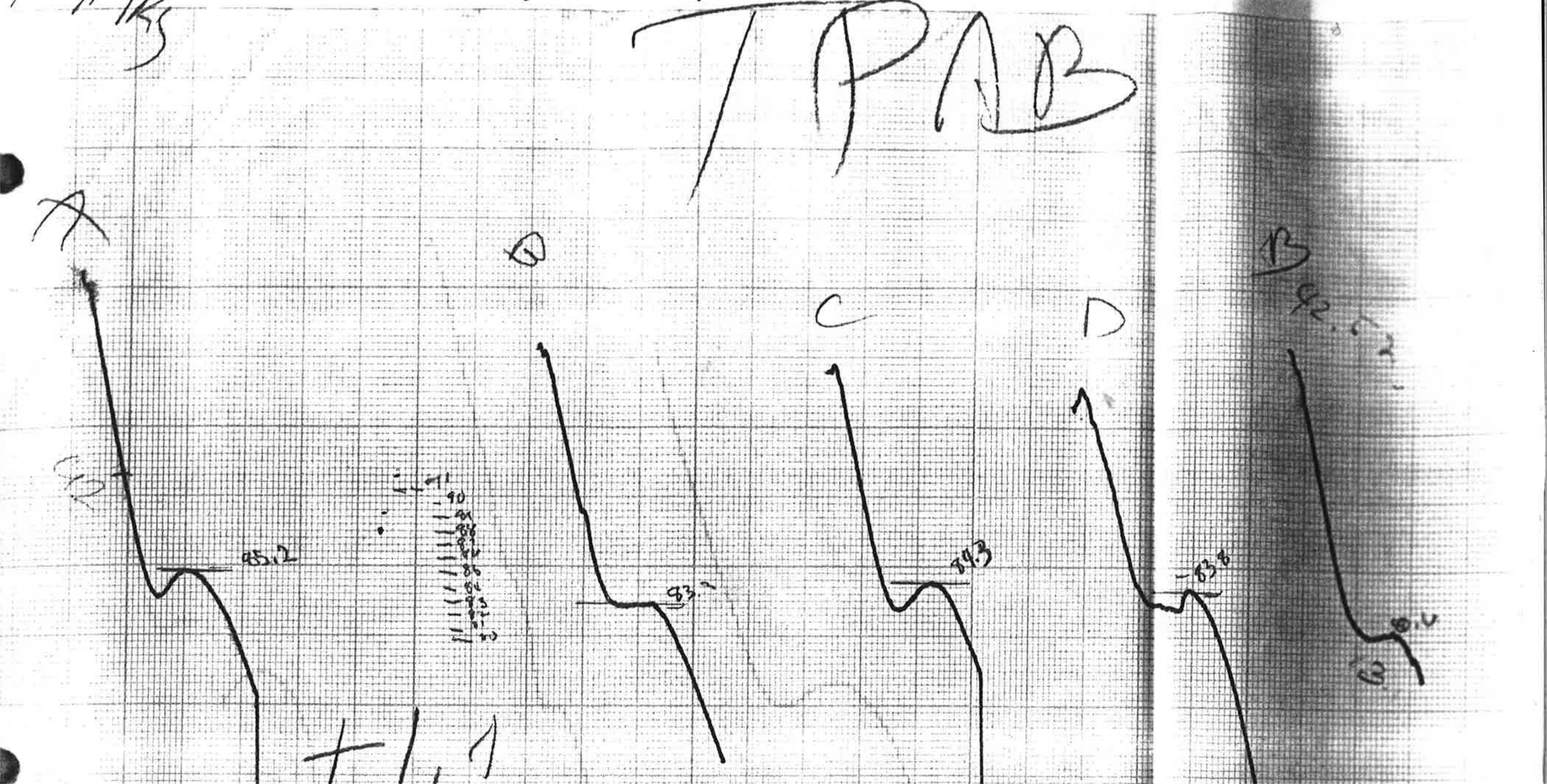


CHART No. CPP20023/00

T-5- Compatibility

41. HRS



T-5-AB compatibility