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CHANGES IN THE ASPHALTENES OF ATHABASCA BITUMEN DURING HYDROCRACKING

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## INTRODUCTION

The asphaltenes which by definition comprise the fraction of bitumen that precipitates by dilution with defined amounts of alkanes, are of major importance during processing of bitumen and heavy oils. They are considered to be the components that give rise to precipitates (often referred to as coke but not the same material as obtained in actual coking) in the reactor that causes operational difficulties. During coking they are considered to be the major precursors of the coke that remains as residue. Coking operations are wasteful because of the large amount of undesirable coke that is produced. During upgrading processes the high molecular weight asphaltenes along with other high molecular weight components have to be cracked to lower molecular weight products. In this report some of the changes that take place in the asphaltenes during non-catalytic thermal hydrocracking are discussed.

The chemical structures of asphaltenes is quite controversial. Yen (1) and to some extent Speight as well as others postulate that the asphaltenes consist of very large stacked polynuclear aromatic structures with large alkyl substitution. More recently, Strausz et al (2) are postulating structures with small hydroaromatic structures joined by sulphide linkages. Reduction of Athabasca asphaltenes with alkali metal in amine was done before in this laboratory (3). Thirty-seven atoms of hydrogen were added per 100 carbon atoms to obtain almost complete desulphurization. The fact that so much hydrogen could be added and the fact that the average molecular weight decreased only to around 2000 from around 6000 does not support Strausz's theory. However according to ultraviolet spectra the polynuclear aromatic structures do not appear to be as large as Yen postulates.

## DISCUSSION

### Weights and Elemental Analyses

There is a steady decrease in the asphaltenes content with an increase in pitch conversion (Figure I). As the asphaltenes are part of the pitch they are gradually degraded. One of the processes occurring is the cleavage of hydrogen-rich alkyl groups from the aromatic clusters. This results in the actual amounts of asphaltenes remaining and the depletion of hydrogen as evidenced by the increase in carbon to hydrogen ratios (Figure II). The nitrogen content increases from 0.83% in the feed to 1.88 in the asphaltenes of the most severely-treated samples (Table I).

### Infra-red Spectroscopy

#### Pyrrolic Groups (3465 $\text{cm}^{-1}$ )

The spectra showing this absorption as obtained in methylene chloride solutions are shown in Figure 3). It can be seen that with increasing pitch conversion there is a steady increase in this absorption. In Table II are the milliequivalents obtained in the asphaltenes of 100 g of hydrocracked products.

#### Aromatic Hydrogen (3050 $\text{cm}^{-1}$ )

These spectra are shown in Figure 4. It can be seen that with increasing severity the absorption at 3050  $\text{cm}^{-1}$  increases particularly at the higher conversion rates. This absorption is due to aromatic hydrogen and therefore it appears that the aromatic hydrogen content in the asphaltenes increases with severity of cracking.

#### Aliphatic Carbon (2800-3000 $\text{cm}^{-1}$ )

The absorption at 2800-3000  $\text{cm}^{-1}$  is due to aliphatic carbon atoms. The absorptivity due to the main peak at 2920  $\text{cm}^{-1}$  changes slightly at the low conversion rate but at the 80% conversion it is reduced substantially (Figure 3). The absorbances for  $\text{lg/l/cm}$  were 1.99, 1.99, 2.12 and 0.90 for asphaltenes obtained from untreated, and from 13%, 26% and 80% converted samples. The other shoulders and peaks in this region appear to follow the same trend. The aliphatic carbon atoms decrease with increasing the severity of hydrocracking.

### Absorption at 1600 cm<sup>-1</sup>

This absorption is shown in Figure 4 in which methylene chloride volumes were used. The absorption in potassium bromide pellets were similar. The absorption peak at around 1600 cm<sup>-1</sup> is due to aromatic carbon atoms but cannot be used for determination of aromaticity. However the absorption at around 1640-1690 cm<sup>-1</sup> is due to carbonyl (keto and amide) groups. As the severity of treatment increases this absorption decreases.

### Absorption at 1200-1500 cm<sup>-1</sup>

The absorption at around 1460 cm<sup>-1</sup> is due to both methylene and methyl groups and this decreases in the asphaltenes of the lower conversion samples, but then appears fairly stable. Absorbances of 0.18, 0.13, 0.10 and 0.12 were found for asphaltenes from untreated bitumen, 13%, 28% and 80% converted bitumen samples respectively. The absorption at 1380 cm<sup>-1</sup> is due to methyl groups and this decreases markedly at 28% conversion and then remains almost constant at higher levels of conversion. The absorption values for the asphaltenes were 0.060 cm<sup>-1</sup>, 0.038 cm<sup>-1</sup>, 0.043 cm<sup>-1</sup> and 0.034 cm<sup>-1</sup> for the same samples.

It is interesting to note that the absorption around 1325 cm<sup>-1</sup> increases with hydrocracking severity. This is usually considered due to isopropyl or other branched alkyl groups which are relatively thermally unstable. Absorption in this region could also be due to polycyclic aromatic groups.

### Absorption at 900-1200 cm<sup>-1</sup>

The untreated asphaltenes have substantial peaks in the vicinity of 1010 cm<sup>-1</sup>, 1033 cm<sup>-1</sup> and 1110 cm<sup>-1</sup>. This absorption is also present in the asphaltenes of the low conversion samples but in the more severely-treated asphaltenes it is diminished quite drastically.

### Absorption at 700-900 cm<sup>-1</sup>

In the untreated asphaltenes there are small absorption peaks at around 755 cm<sup>-1</sup>, 815 cm<sup>-1</sup> and 865 cm<sup>-1</sup> (Figure 5). These peaks increase in intensity with increasing the severity of hydrocracking, especially at the highest conversion rate. Absorption in this range is largely due to hydrogens attached to aromatic structures. The peak at 863 cm<sup>-1</sup> can also be

ascribed to lone hydrogen atoms attached to the aromatic structures. The peaks at  $815\text{ cm}^{-1}$  might be due to pairs of adjacent hydrogen atoms while the peak at  $755\text{ cm}^{-1}$  due to groups of three adjacent hydrogen atoms. The untreated asphaltenes show smaller peaks at  $700\text{ cm}^{-1}$  which might be ascribed to groups of four adjacent hydrogen atoms. However this peak diminishes with increasing the severity of treatment.

There is also a shoulder at  $724\text{ cm}^{-1}$  in the untreated asphaltenes which disappears in the more severely treated samples. This peak is due to straight alkyl groups with more than four carbon atoms. These long alkyl groups appear to be cleaved from the aromatic structures during treatment.

The fact that the aromatic hydrogens appear to increase in the asphaltenes can be interpreted. The increase in aromatic hydrogen content increases in about the same proportions as the decrease in the amount of asphaltenes. Thus if the structures with the aromatic hydrogens are not degraded then the concentration effect would explain this increase. Another explanation is that as the original asphaltenes become converted more asphaltenes are formed due to cleavage of alkyl groups from other large aromatic structures causing them to be insoluble in pentane. Alkyl groups might be cleaved directly from the aromatic structures and replaced by hydrogen. This is assumed not to take place in non-catalytic thermal hydrocracking. Cycloalkyl groups might also become aromatized and give rise to more aromatic hydrogen in asphaltenes.

#### Absorption at $400-700\text{ cm}^{-1}$

There is considerable absorption in this region of the asphaltenes precipitated from the untreated bitumen. Two large peaks appear at  $540\text{ cm}^{-1}$  and  $480\text{ cm}^{-1}$  and a relatively small peak at  $435\text{ cm}^{-1}$ . These peaks survive the less severe treatments but disappear with the more severe conditions. The two peaks at the lower frequencies might be due to aromatic disulphides. The higher one might be due to alkyl disulphides.

Some polynuclear aromatic hydrocarbons also absorb in this region but the fact that these peaks disappear on hydrocracking makes this possibility not very likely.

REFERENCES

1. Yen, T.F. Energy Sources; VI p. 447; 1974.
2. Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P. "The chemical composition of Athabasca bitumen", Hydrocarbon Research Centre, Department of Chemistry, University of Alberta, Edmonton, Alberta.
3. Sawatzky, H. and Montgomery, D.S. "The reduction of asphaltenes", Fuel Journal E 57, p. 001.

TABLE 1

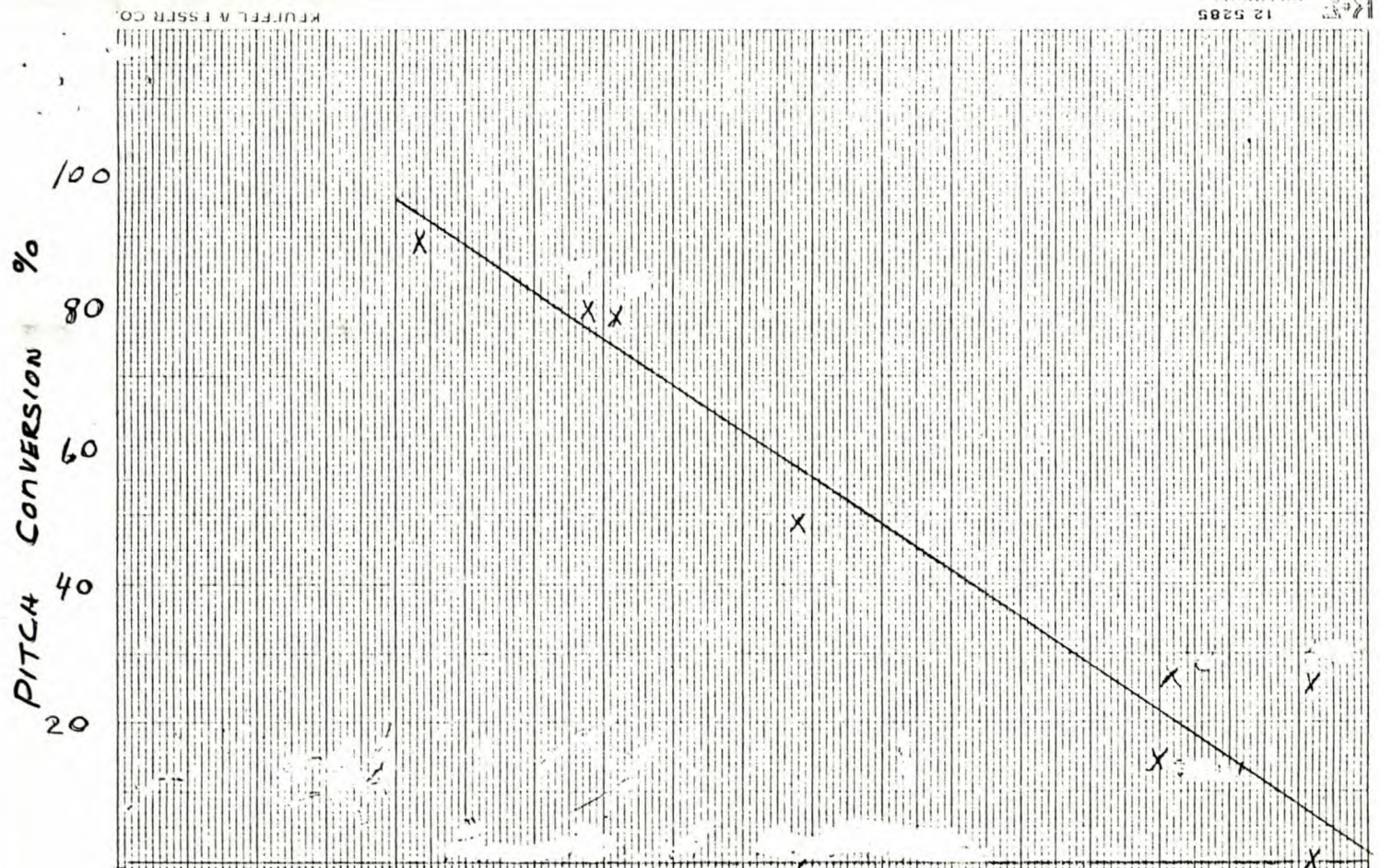
Distribution of Total Nitrogen Content  
in Hydrocracked Athabasca Bitumen Products  
Nitrogen Content, wt. %

Sample Number	C <sub>5</sub>	A <sub>2</sub> (86-1-1)	Bottoms 'C'	6	8
Pitch Conv.	Feed	15%	28%	59%	80%
Asphaltenes	.83	1.25	1.28	1.45	1.88

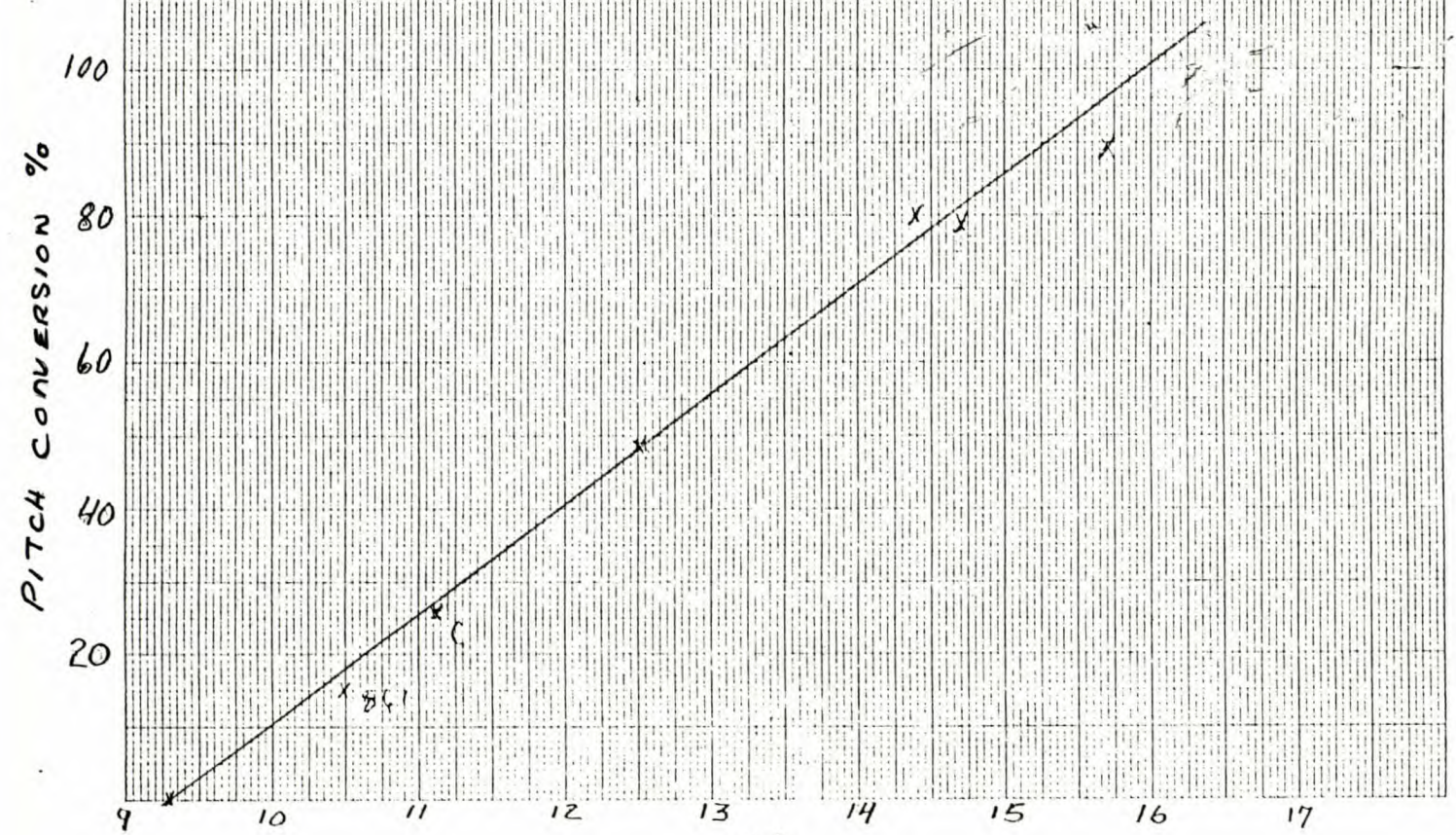
TABLE 2

Milliequivalents of Pyrrolic Compounds  
in 100 grams of the Hydrocracked Samples

Sample Number	C <sub>5</sub>	A <sub>2</sub>	Bottoms 'C'	6	8
Pitch Conv.	Feed	15%	28%	59%	80%
Asphaltenes	3.30	4.10	3.65	7.43	7.90



Amounts of - ASPHALTENES  
FIGURE 1



C/H  
FIGURE 2



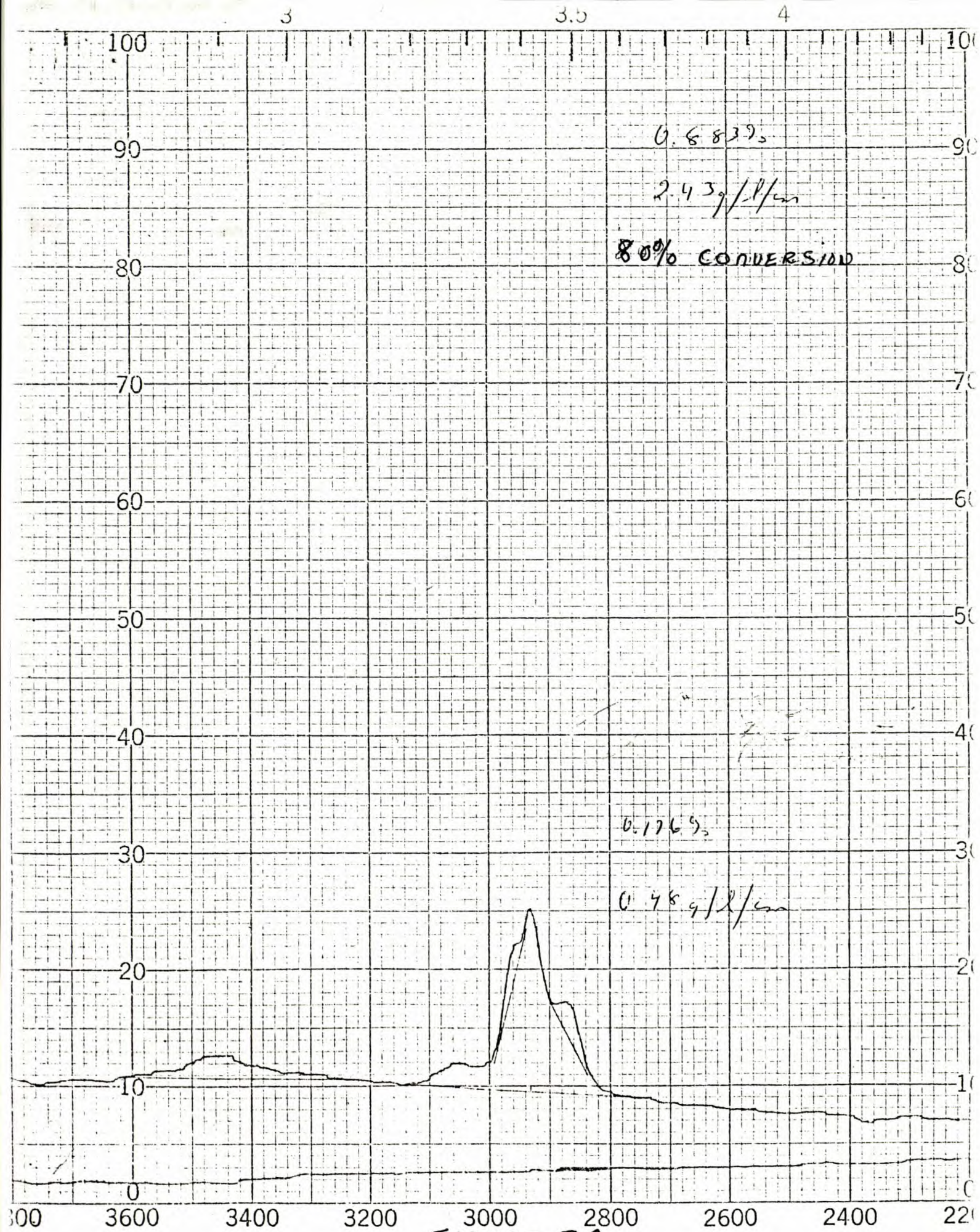
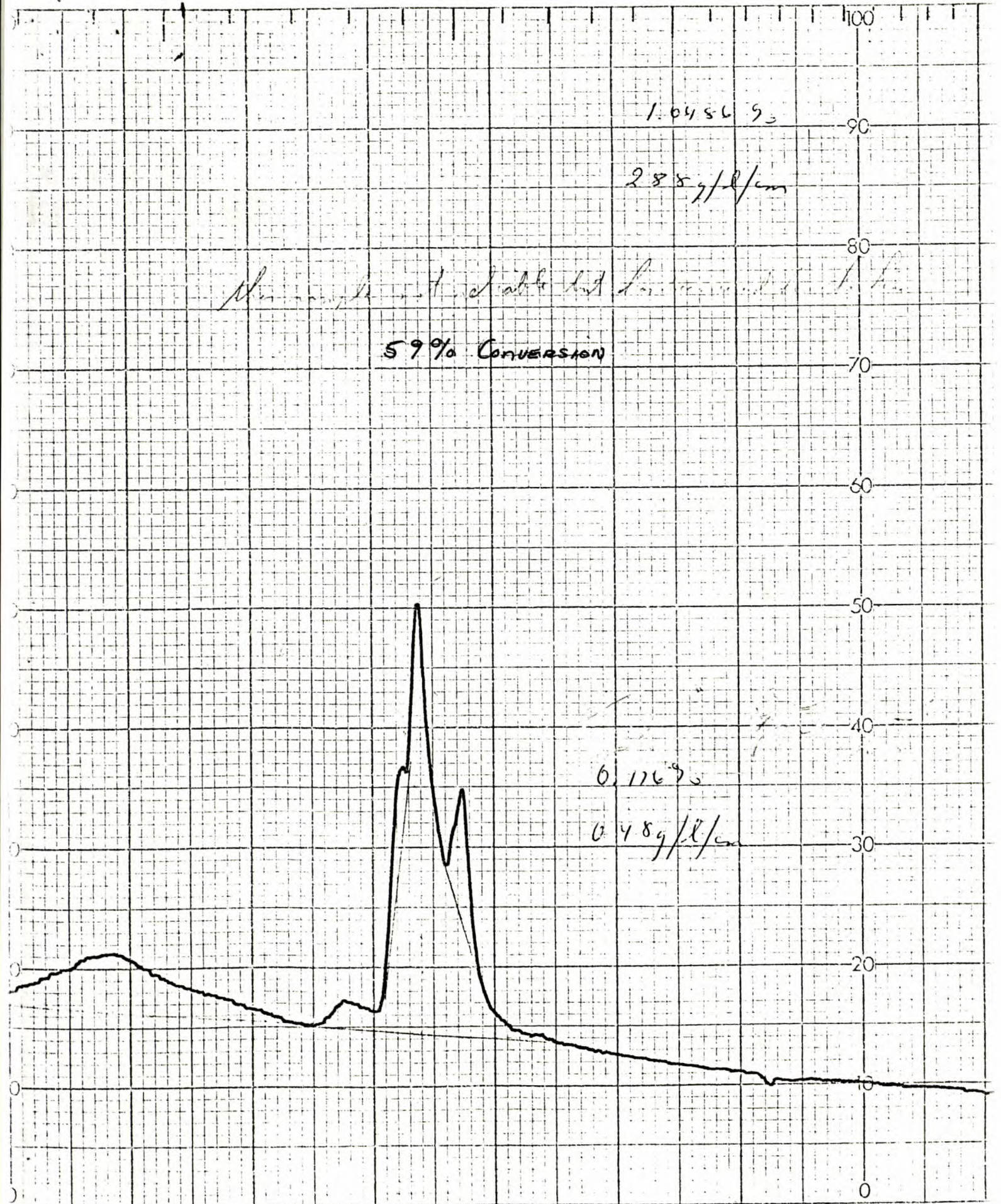


FIGURE 3A



59% Conversion

1.0456 g

2.88 g/l/cm

0.176 g

0.48 g/l/cm

The sample is stable and...

FIGURE 3B

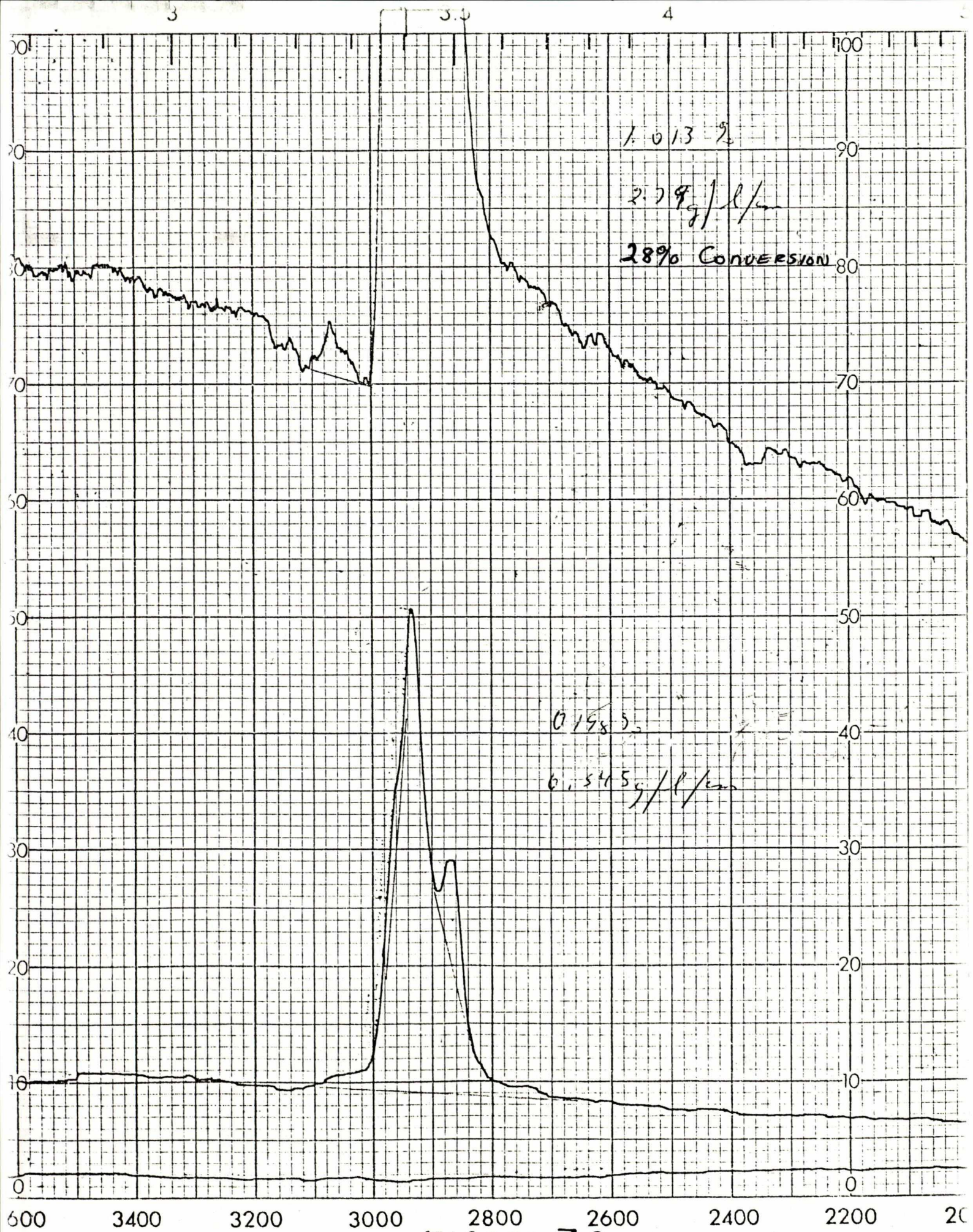


FIGURE 3C

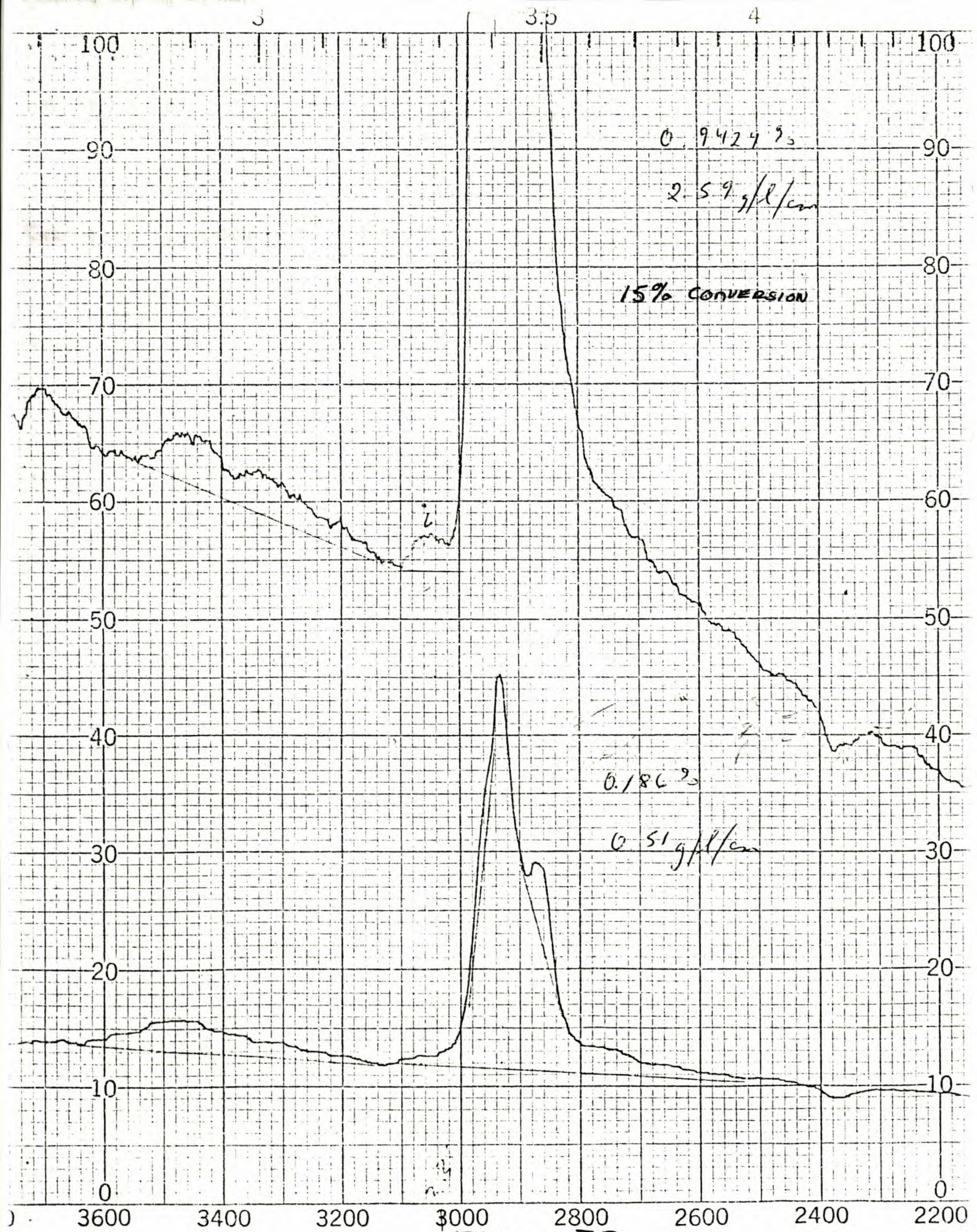


FIGURE 3D

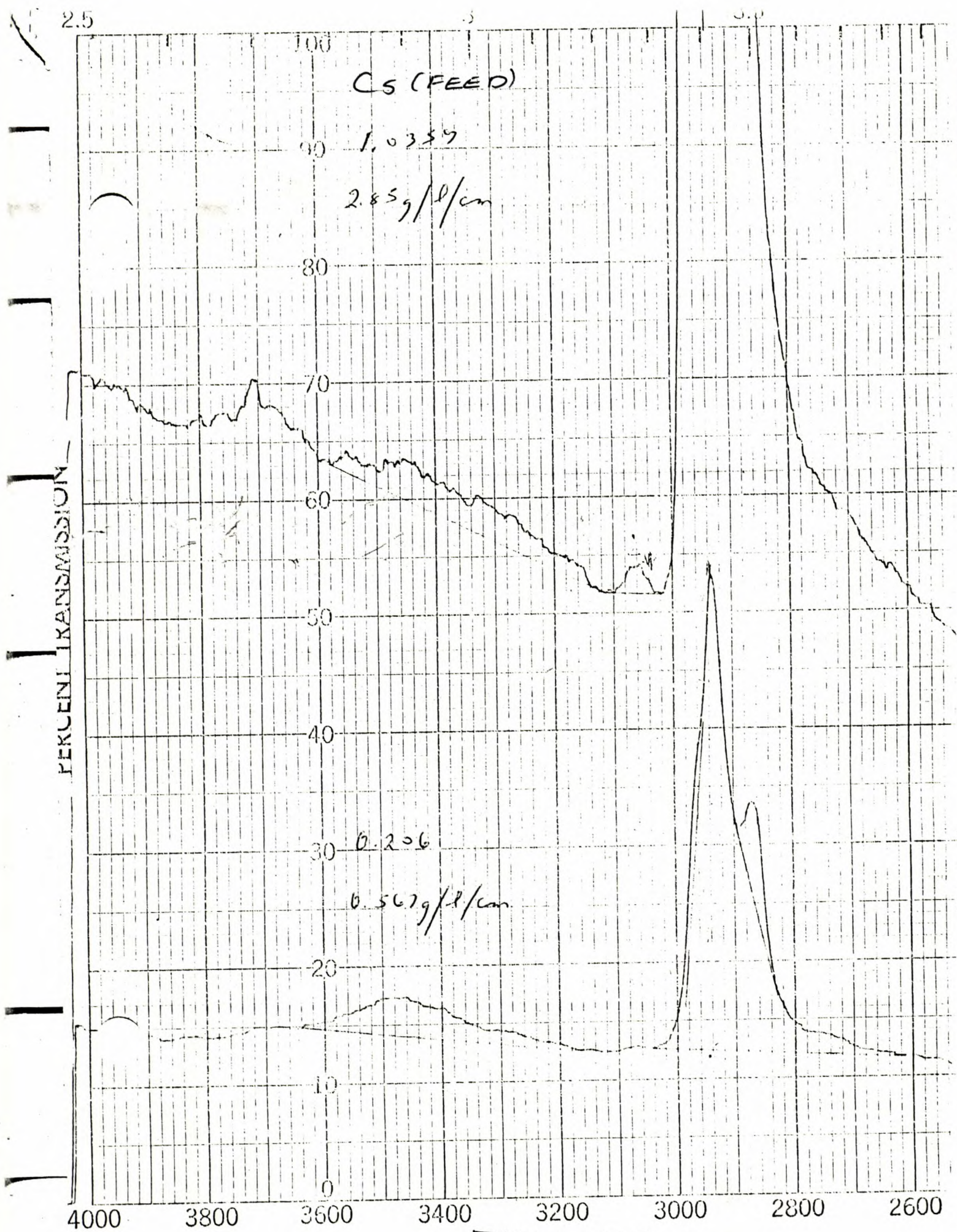


FIGURE 3E

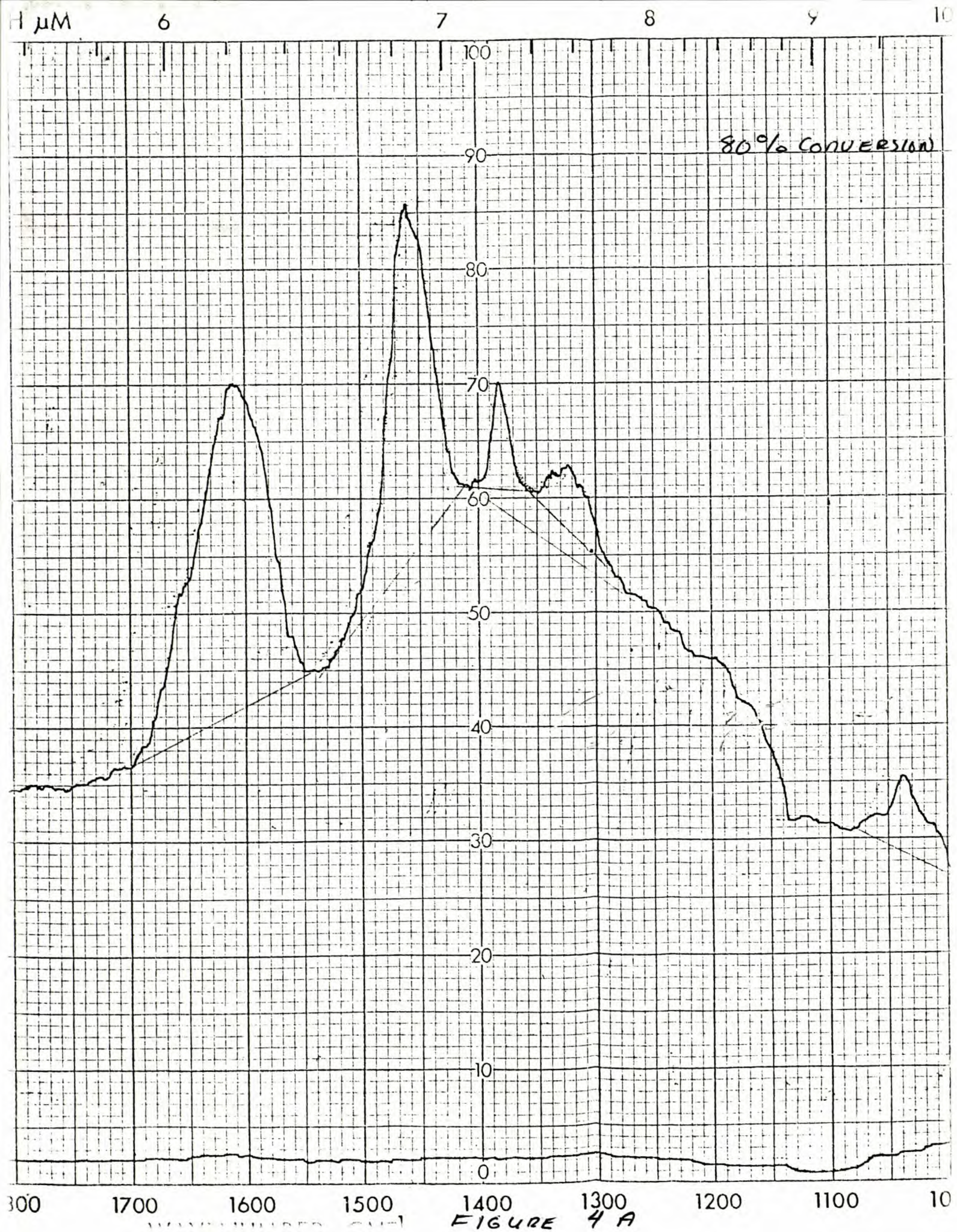
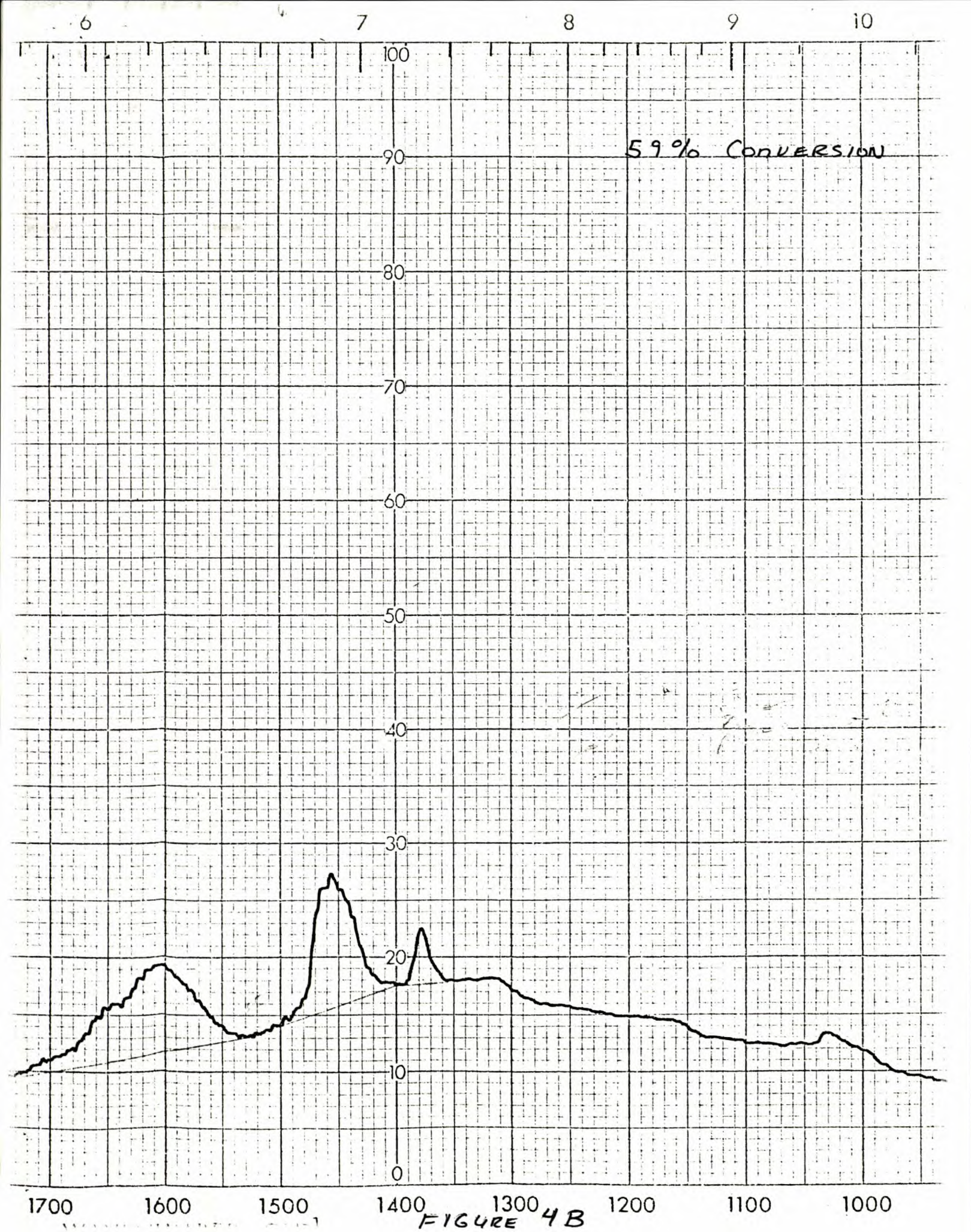


FIGURE 4 A



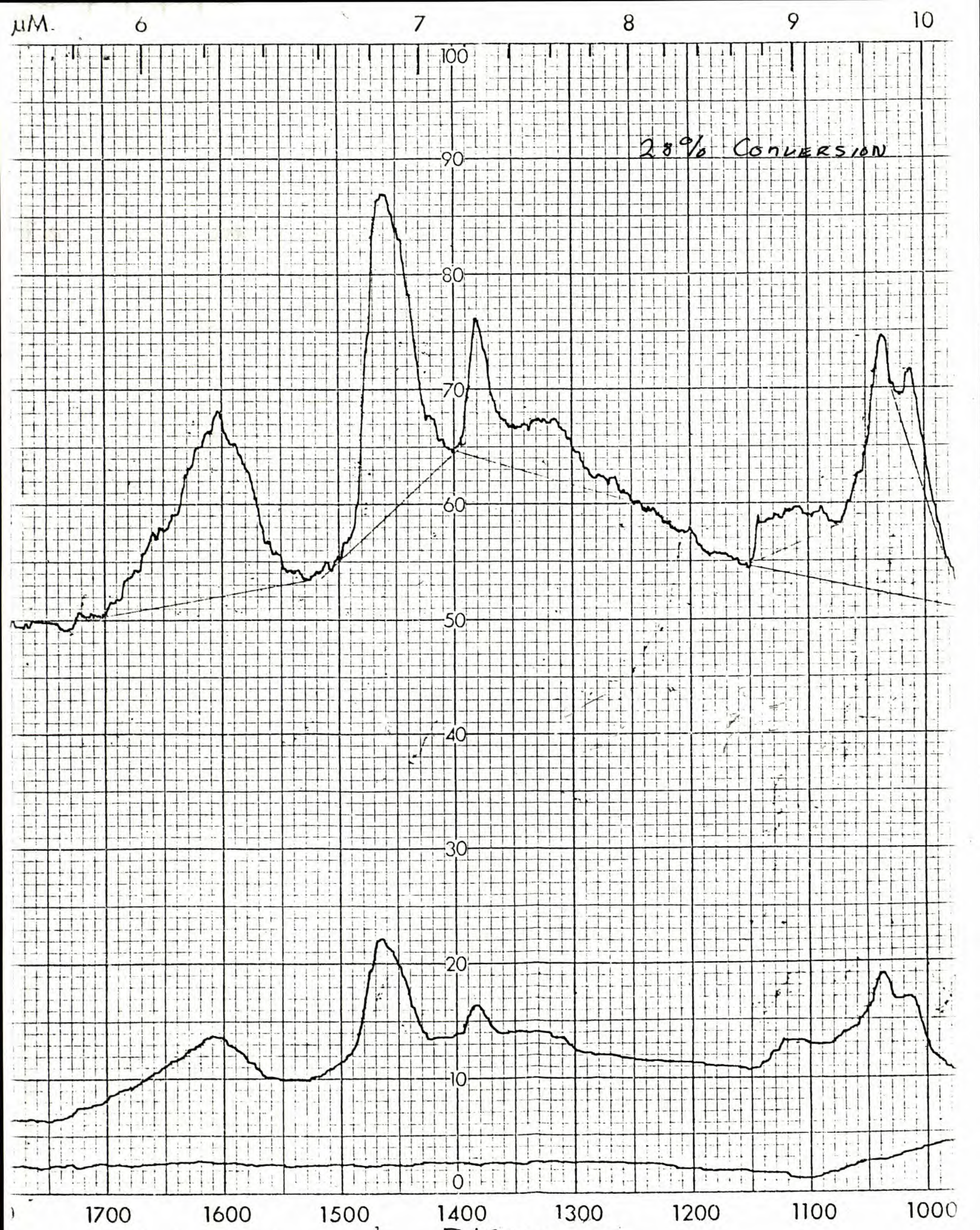


FIGURE 4C



WAVELENGTH IN MICRONS

6

7

8

9

10

15% CONVERSION

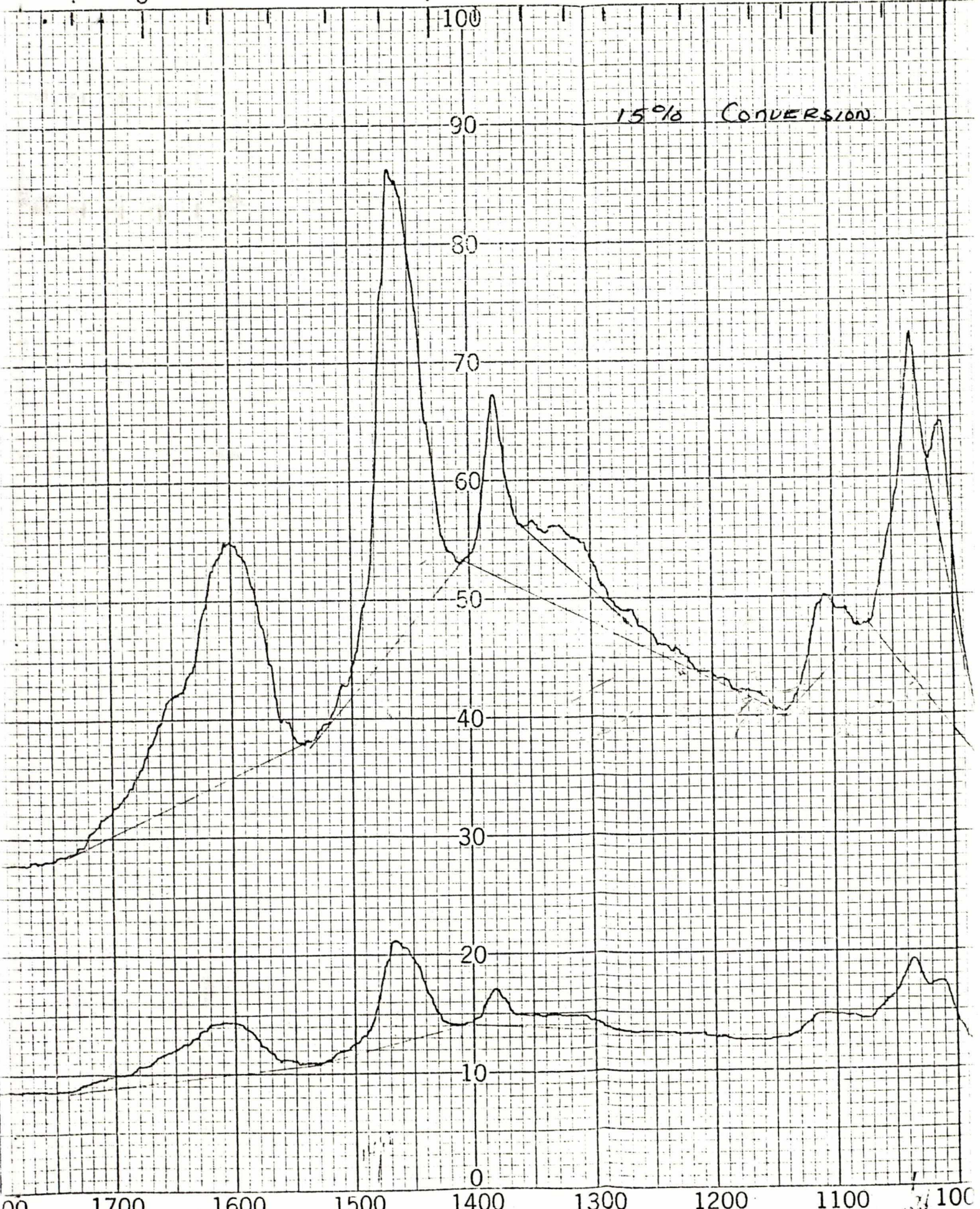
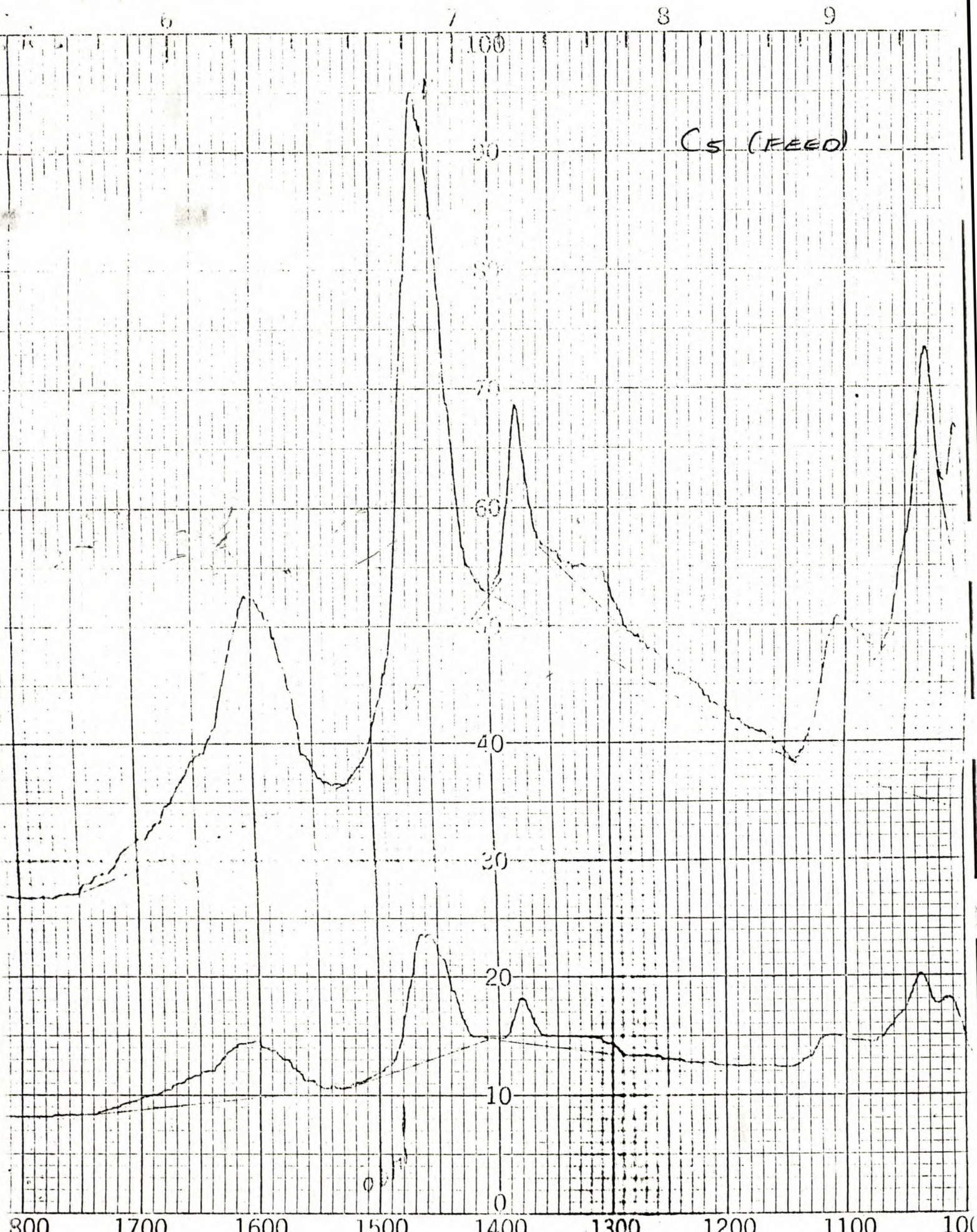
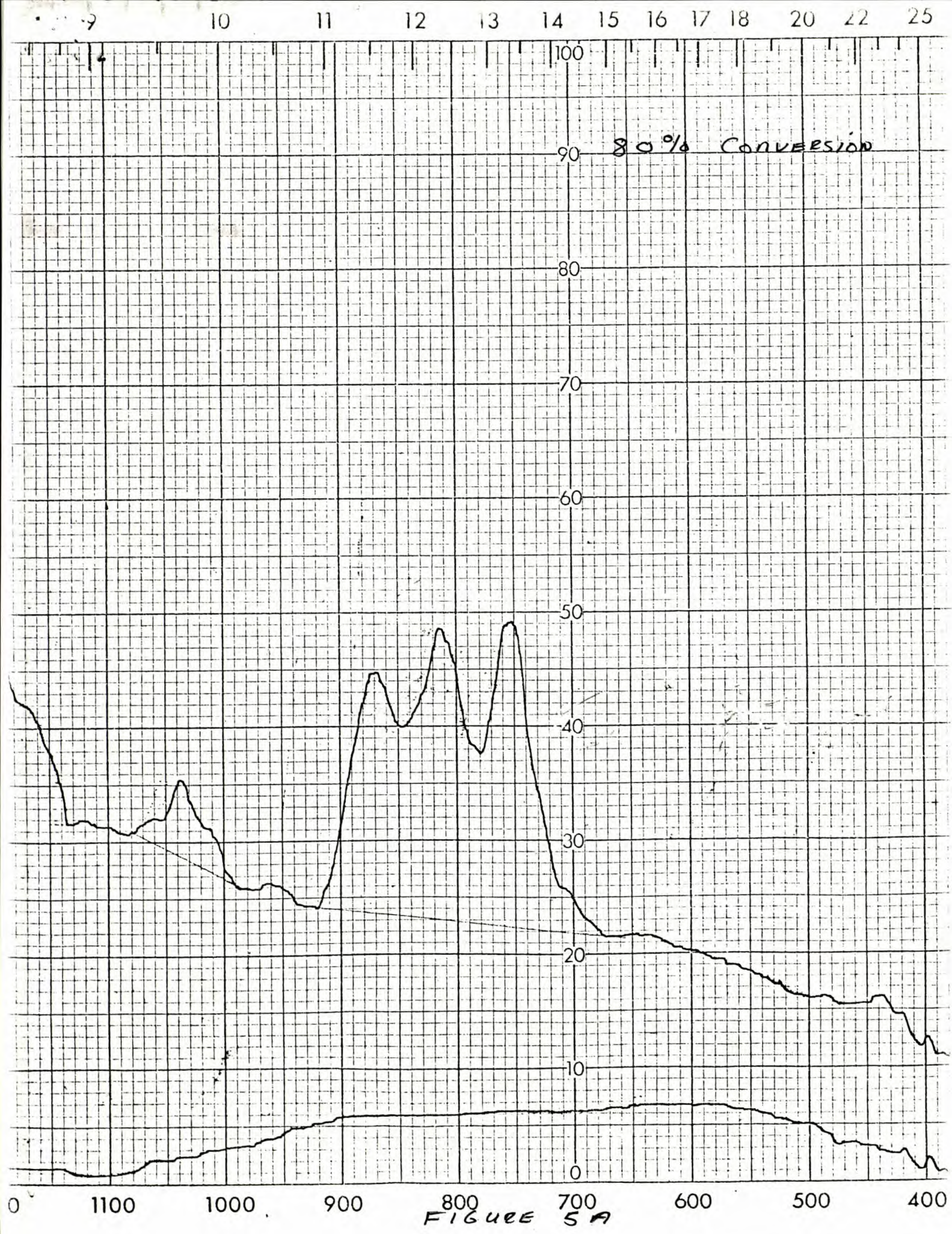


FIGURE 4D



WAVENUMBER  $\text{CM}^{-1}$  FIGURE 4 E



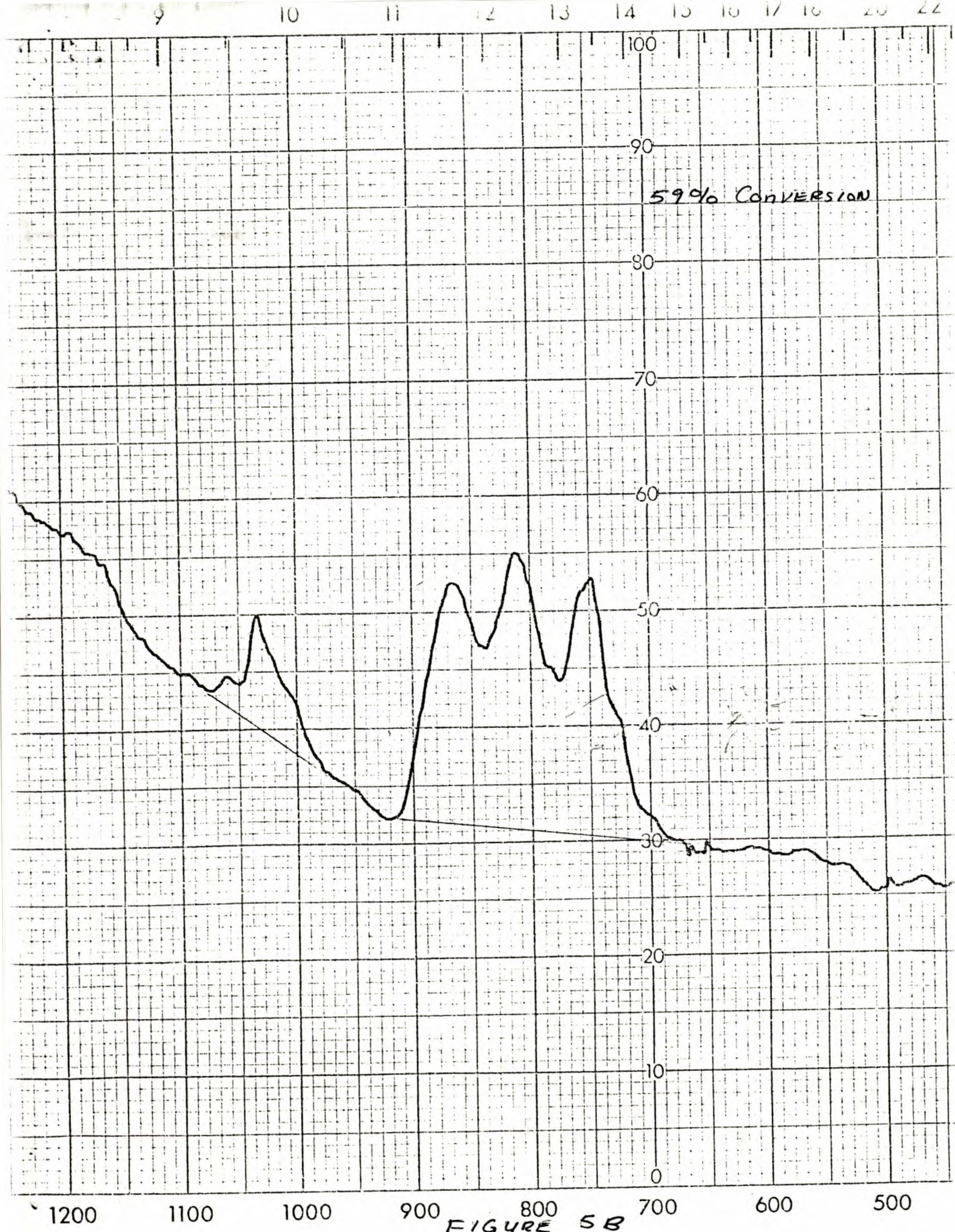


FIGURE 5B

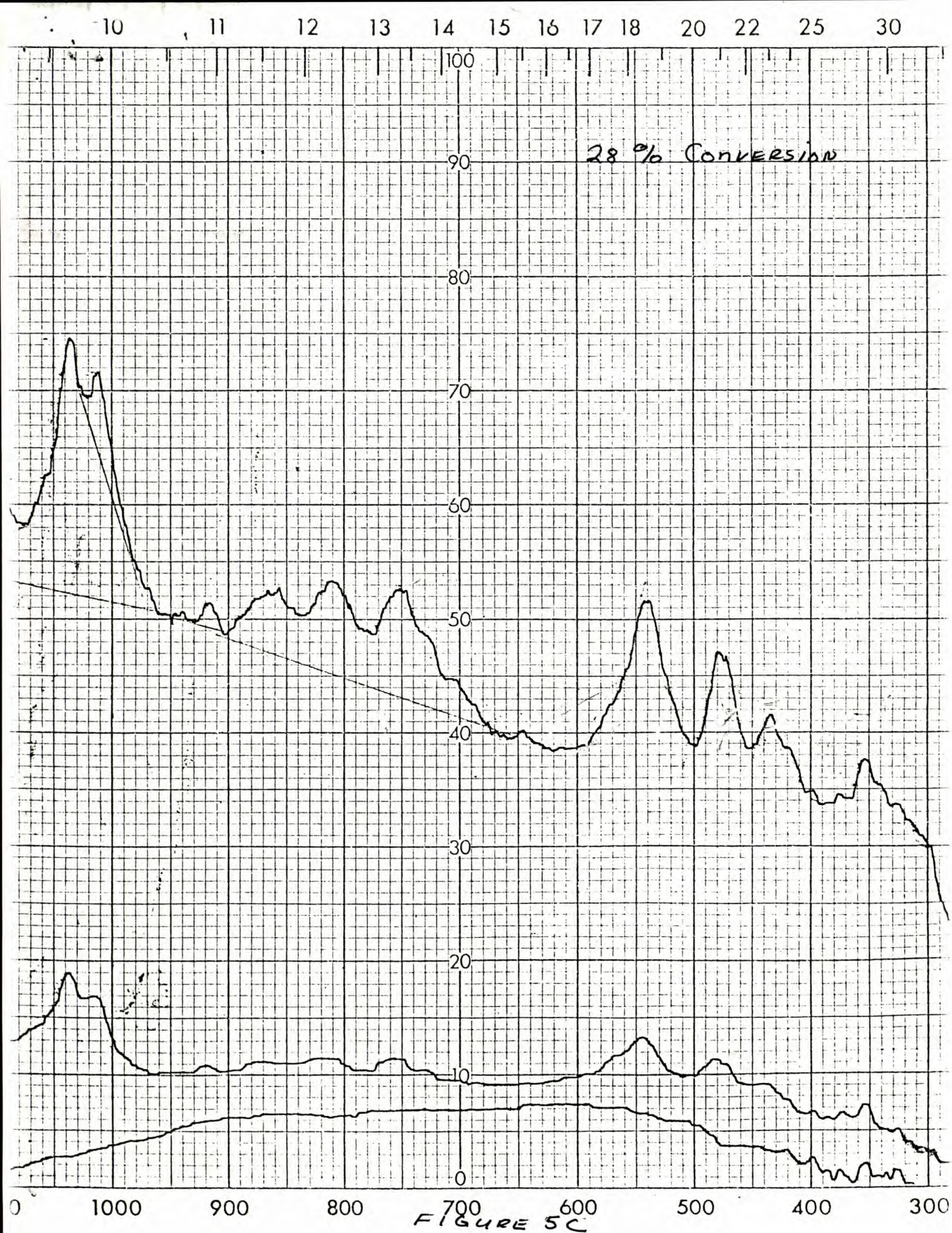
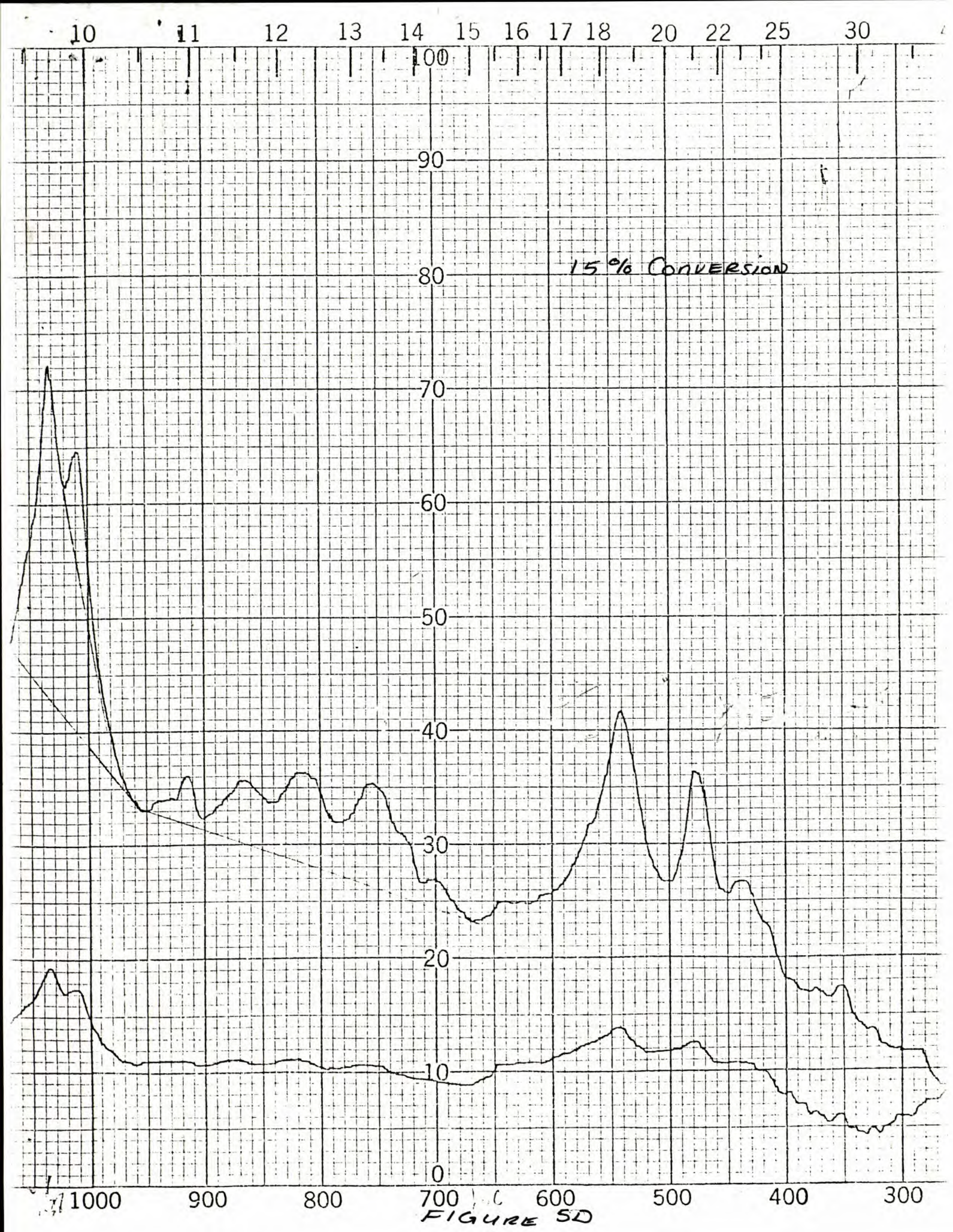


FIGURE 5C



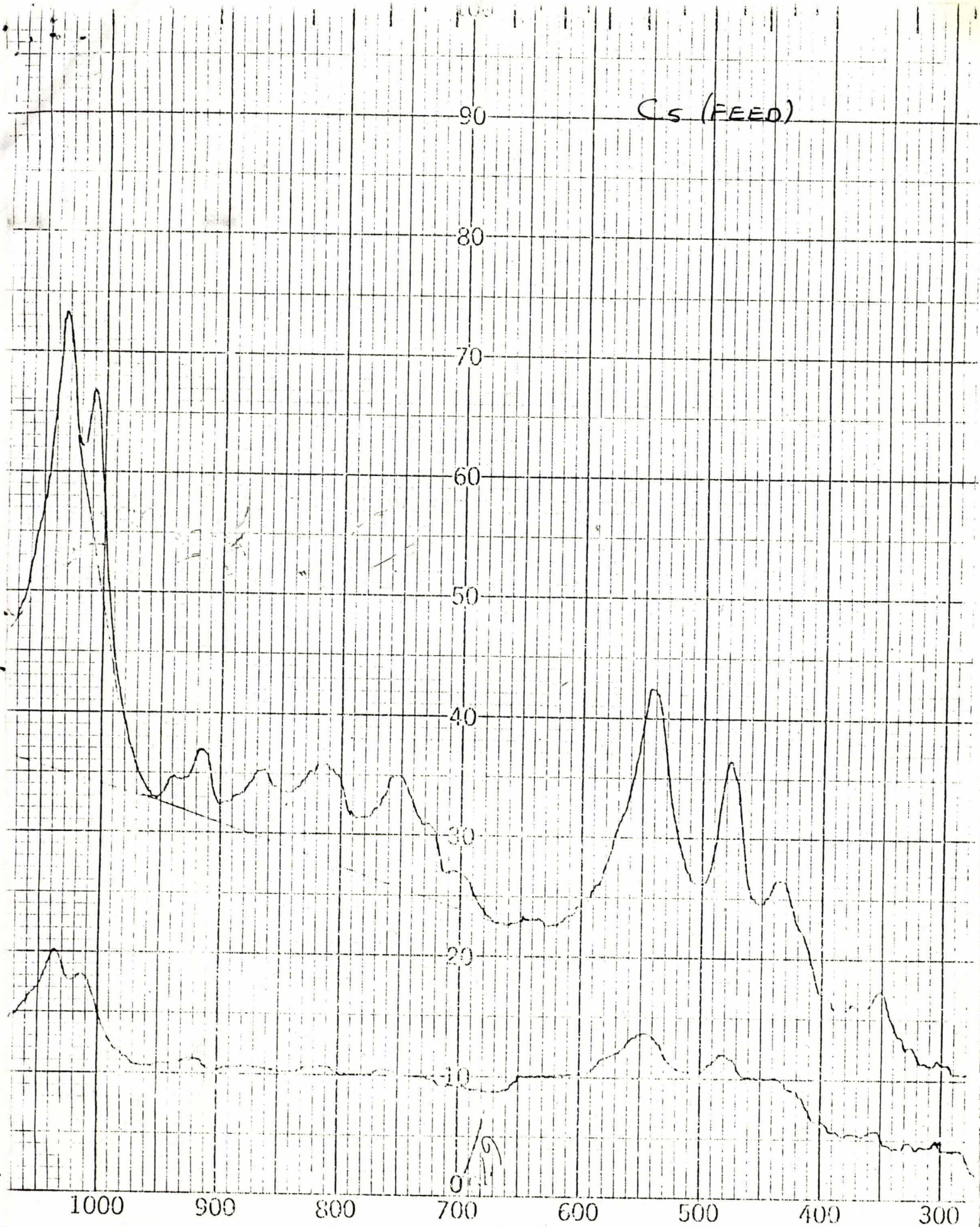


FIGURE 5 E