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Date?

EXPERIMENT 1: FOURIER TRANSFORM ANALYSIS OF OSCILLATING CHEMICAL REACTIONS

ABSTRACT

The Fourier transform is a technique that has become of widespread use throughout all areas of chemistry and other sciences. In this experiment, the period of oscillation of the Belousov-Zhabotinskii reaction was studied by use of a Fourier transform. Absorbance data was collected as a function of time and after transformation, high frequency noise was eliminated from the frequency domain. An inverse transform provided a spectrum which was much more easily interpreted and the period of oscillation with uncertainty was determined to be 25 (± 7) seconds. This report will discuss the methods used to arrive at this conclusion.

↳ You also may mention that your results match up with those found in literature.

INTRODUCTION

The Fourier transform is a mathematical operation spanning many areas of chemical research, including data analysis and spectroscopy. Its importance lies in its ability to convert data in the time domain to the frequency domain. The Fourier transform has become of great importance, especially with the development of computers with faster processors. Fourier transform (FT) spectrometers have replaced older styles of instruments due their ability to obtain spectra in a more time efficient and precise way. For example, in NMR spectroscopy, older continuous wave instruments scanned a range of frequencies to obtain a spectrum. This is analogous to a specific frequency of sound causing an object such as a vase to vibrate. Newer FT instruments use a single pulse to excite all frequencies at once. This is analogous to a sonic boom causing all objects in an area to vibrate. This pulse is centered about a specific frequency and covers a range of frequencies, the spectral width. The receiver signal is monitored as a function of time to obtain a free induction decay pattern which is then changed, via a Fourier transform, to the frequency domain.

In this experiment, a slightly different application of a Fourier transform was studied through the Belousov-Zhabotinskii (BZ) reaction. The BZ reaction is an oscillating chemical reaction, and can be shown to be analogous to the Oregonator model of this type of phenomena. The concentrations of certain species vary periodically with time while others are converted irreversibly to products, providing the free energy difference that drives the chemical process. In the BZ reaction, an acidic bromate solution irreversibly brominates malonic acid with use of a cerium catalyst. The bromination is coupled to an oxidation-reduction cycle involving $\text{Ce}^{3+}/\text{Ce}^{4+}$. Use of a ferroin indicator made the $\text{Ce}^{3+}/\text{Ce}^{4+}$ oscillations viewable through color changes from red to blue, allowing the reaction to be studied through spectroscopy. A helium-neon laser was used to measure the oscillating absorbance of red light by the reaction mixture. Data was collected in the time-domain and converted, via a Fourier transform, to the frequency domain. At this point, some of the high frequency "noise" was truncated to remove it from the spectrum and an inverse Fourier transform used to obtain a filtered time-domain plot of the oscillating component. The data were truncated at several frequencies and the effect on the spectrum observed. Once a clean spectrum was obtained, the period of oscillation was determined and analyzed in comparison to accepted values.

EXPERIMENTAL

The reaction was performed according to the specifications provided by Eastman.¹ A solution of malonic acid (4.6 g), potassium bromate (1.6 g), ceric ammonium nitrate (0.1626 g) and ferroin indicator (2 ml) in water (135 ml) was prepared and the reaction initiated by the addition of

↳ Was it really 2ml?

¹ M.P. Eastman, G. Kostal, and T. Mayhew, "An Introduction to Fast Fourier Transformations through the Study of Oscillating Reactions," *J. Chem. Ed.* 63, 453 (1986).

concentrated sulfuric acid (12.5 ml). Appropriate safety conditions were maintained during the exothermic addition steps to prevent possible fires or spills.

Light from a helium-neon laser ($\lambda=632.8$ nm) was used to measure the absorbance of red light from the solution as the reaction proceeds. The laser light was passed through the solution and absorbance measured by a detector. Vigorous stirring was also necessary to maintain a homogeneous mixture. The ferroin indicator caused the reaction mixture to appear blue during the oxidative stage and red during the reductive stage. Data points measuring absorbance were collected at intervals of 0.1 seconds until 1024 data points were obtained. This procedure was repeated for five successive trials, in the last of which, 2048 data points were obtained.

Once data were collected, the program "Newerfourier" was used to transform the data into the frequency domain. The program was used to truncate the frequency domain at several different values (4, 8, 16, 32, 64, and 128) for each trial, and then to back transform to the time domain. The program "Kaleidagraph" was then used to generate graphs of absorbance versus time for the data from each trial and to determine the times at which maxima and minima were reached in each trial in order to determine the period. Finally, "Kaleidagraph" was used to generate a graph of the real portion of the Fourier transform versus the frequency.

RESULTS & ANALYSIS

The program "Kaleidagraph" located in the MacChemLab/in Remsen Hall was used to generate graphs of the data truncated by the program "Newerfourier," located on the same computers. For trials one through four, truncation at the value of four generated a graph from which period could easily be determined. For trial five, truncation at the value of eight provided an acceptable graph. In this trial, truncation at four eliminated necessary data points, making the graph unreadable. Figures I-III show the plots generated for several trials. They are shown before and after truncation, with expansions of data used in analysis. Table I (next page) summarizes the data collected for each trial.

Once the minima and maxima were obtained, the period of oscillation could be determined. This was accomplished through simple subtraction between the adjacent maxima and adjacent minima to obtain τ , the period of Ce^{3+}/Ce^{4+} oscillations in the BZ reaction. These findings are shown in Table II (next page).

It can be seen in the data that few irregularities are present, most notably the value of 11.6 seconds obtained in trial 4. The graph generated for trial 3 was also difficult to interpret, as only two maxima and one minimum could be seen. Possible causes of these irregularities will be discussed in the analysis section.

The statistical analysis software of a TI-89 graphing calculator was used to analyze the data. Trials 3 and 4 were not used in analysis due to the difficulty in interpreting the data in these trials. A histogram generated showed that the data from trials 1, 2, and 5 can be treated as a Gaussian, or normal, distribution. Therefore, the mean and standard deviation could be used in the error analysis. Equation (1) was used to calculate the mean, which was taken at τ_{best} . Equation (2) was used to calculate the standard deviation.

$$\bar{x} = \frac{\sum x_i}{N} \quad (1)$$

$$\sigma_x = \sqrt{\frac{1}{N-1} \sum (x_i - \bar{x})^2} \quad (2)$$

where N is the total number of data points.

This data is unnecessary to present since you explain how you did it.

Trial	Maxima		Minima	
	Time (seconds)	Absorbance	Time (seconds)	Absorbance
1	14.9	0.89090	9.3	0.88780
	42.8	0.91240	28.6	0.85550
	71.5	0.97300	56.1	0.85630
	95.3	0.94350	82.8	0.90690
2	22.4	0.82950	7.9	0.80500
	44.7	0.84900	28.5	0.82760
	69.4	0.86239	53.8	0.84360
	90.9	0.88920	75.8	0.86010
3	44.5	0.66960	58.8	0.65850
	72.4	0.66360	80.5	0.66220
	94.0	0.66960		
4	23.6	2.0031	9.0	1.8967
	53.8	1.9994	37.5	1.9191
	65.4	1.9899	65.0	1.9880
	96.5	2.0028	83.1	1.9400
5	21.9	1.6178	8.5	1.5557
	48.8	1.6235	34.2	1.5787
	72.9	1.6445	58.0	1.6124
	97.6	1.6772	81.5	1.6364
	120.9	1.6863	108.8	1.6611
	150.8	1.6761	134.6	1.6542
	168.8	1.7223	151.0	1.6751
195.5	1.7058	183.5	1.6582	

Table I: Summary of the maxima and minima of the absorbance versus time plots for each trial

Trial	Maxima		Minima	
	Interval	τ	Interval	τ
1	1	27.9	1	19.3
	2	28.7	2	27.5
	3	23.8	3	26.7
2	1	22.3	1	20.6
	2	24.7	2	25.3
	3	21.5	3	22.0
3	1	27.9	1	21.7
	2	21.6		
4	1	30.2	1	28.5
	2	11.6	2	27.5
	3	31.1	3	18.1
5	1	26.9	1	25.7
	2	24.1	2	23.8
	3	24.7	3	23.5
	4	23.3	4	27.3
	5	29.9	5	25.8
	6	18.0	6	16.4
	7	26.7	7	32.5

Table II: Obtained values for period of oscillation shown by trial

In this experiment, a 95% confidence range was desired. In other words, the experimenter wanted to be sure that there was a 95% chance that the true value of the period fell in the range denoted by $\delta\tau$. Taking advantage of the properties of a Gaussian distribution, it can simply be stated that $2\sigma_x = \delta\tau$. ✓ good.

The results of the calculation are as follows:

$$\bar{x} = 24.57307; \sigma_x = 3.57411$$

Therefore, using the proper number of significant figures, the final value obtained for the period of oscillation of the Belousov-Zhabotinskii reaction can be stated as:

$$\begin{aligned} \tau \pm \delta\tau &= 25 (\pm 7) \text{ seconds} \\ &= 25 \text{ seconds} \pm 28\% \end{aligned}$$

 ✓

As stated previously, we can be 95% certain that the true value for the period of the reaction lies in this range. In calculation of this uncertainty, propagation of the error in the time the reading was taken was not accounted for. This is because of the precision of the instrument. The data indicates an accuracy of four significant figures in the time value. The error associated with this is extremely small and calculations indicate that the contribution to the overall error would be far less than one percent. Thus, it was not included in error calculation. ✓ good.

Figures IV-VII show plots of the real FT coefficients versus the frequency for three trials. Clearly the frequency of BZ oscillation was quite low, as evident by the visible oscillations. Thus, the high frequency components of this plot can be attributed to noise. Truncation to eliminate all data above certain frequencies provided graphs that were far more easily interpreted. The offset plots in Figures I-III of absorbance versus time after truncation at various values clearly show that as more high frequency noise is eliminated, the plot becomes far smoother and easier to interpret. The pure frequency data, however, presented a fair amount of difficulty in interpretation, as the frequencies observed did not conform well to the inverse relationship between period and frequency. This fact illustrates the usefulness of a Fourier transform. In these plots, the several frequencies at which the ReFFT value was a maximum can be seen. Table III presents the first few frequency maxima observed for various trials, as well as the inverses of these values, as period is the inverse of frequency. For each trial, there is a frequency value which provides a period within the range calculated above. For each of the frequency values that provide a period within the range above, the data shows another maximum at two and three times the frequency value. These data are not shown in the table (they are seen in the plots), but these additional peaks at double and triple values provide strong evidence for the validity of the peaks as representing the actual frequency of oscillation. The reason for this is that the true frequency value will show harmonics, or overtones, at multiples of the value, much in the way that in infrared spectroscopy, an overtone of a bond vibration can be seen at double the wavenumber. Finally, values can clearly be seen that correspond well to the 30 mHz value reported by Eastman.¹ Possible sources of error leading to noted deviations are explained below. ✓

you can ignore these
↓

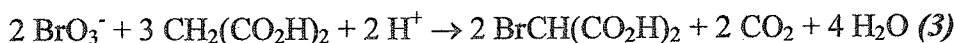
Trial	Frequency (Hz)	Period (s)	Frequency (Hz)	Period (s)	Frequency (Hz)	Period (s)
1	0.0098	102	0.029	34	0.049	20
2	0.0098	102	0.049	20	0.078	13
3	0.029	34	0.049	20	0.068	15
4	0.0098	102	0.029	34		
5	0.0098	102	0.024	42	0.039	26

Table III: Frequency maxima obtained from ReFFT vs. frequency plots

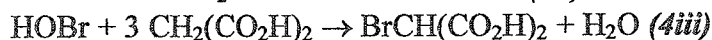
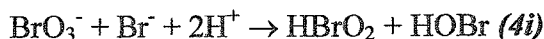
DISCUSSION AND CONCLUSIONS

The Belousov-Zhabotinskii reaction is a typical example of an oscillating chemical reaction. Examples of oscillations are seen in biological systems, electrode reactions, periodic precipitation phenomena, gas reactions, and other places throughout chemistry and physics. Many such reactions are closely related to the Oregonator model of oscillating chemical reactions. The BZ reaction is one of them. This reaction is very sensitive to concentration and can take different paths as the reaction proceeds. For this reason, the overall equation differs slightly between the paper by Noyes and Field² and the paper by Eastman¹, et al.

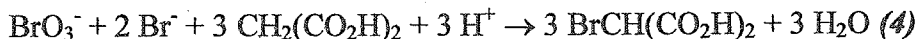
The overall equation for the BZ reaction can be shown to occur as follows.



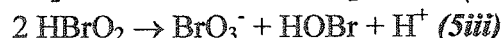
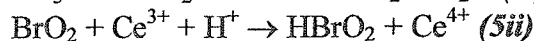
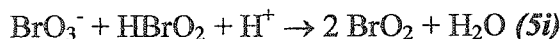
indicate the Ce redox pair in over all rxn. ✓
The reaction can be divided into three distinct steps. The first step consists of three parts.



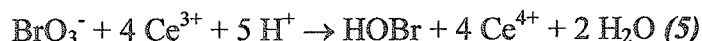
The overall reaction for this step, which can be compared directly to the Oregonator mechanism, can be written as follows.



The second step also consists of three parts.

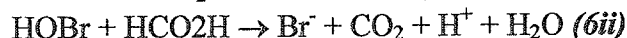
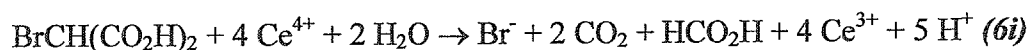


The overall reaction for this step to be paralleled to the Oregonator model can be shown to be the following.

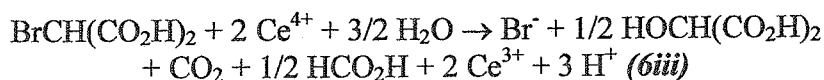


² R.M. Noyes and R.J. Field, "Mechanisms of Chemical Oscillators: Experimental Examples," *Accts. Chem. Res.* 10, 273, (1978). ✓

The next step of the reaction is concentration dependent. If malonic acid is present in stoichiometric deficiency with respect to bromate, the following sequence of reactions is seen.

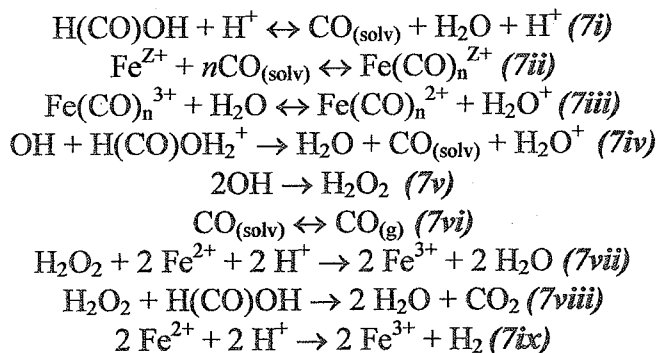


These reactions combined with those of the first two steps provide the overall equation of the BZ reaction (3). The concentration sensitivity of the BZ reaction is explained by this step especially. Malonic acid reacts preferentially with cerium (IV). Thus, if malonic acid is present in excess, the following reaction is seen in place of the two shown immediately above, leading to a different overall stoichiometry.

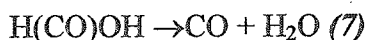


Overall, this reaction is very interesting and worthy of study. It is surprising that a reaction so kinetically complex has a relatively simple period that can be studied. There are many other oscillating chemical reactions known, most of which have parallel kinetic complexity. The Bray-Liebafsky reaction, for example, is an oscillating reaction in which an iodate-iodine complex catalyzes the decomposition of hydrogen peroxide. Early in the study of this reaction, periods of rapid oxygen evolution and alternating formation and destruction of molecular iodine were observed. The mechanism for this reaction is complex and will not be reproduced here, but is easily located.²

Another oscillating mechanism is known as the Morgan reaction. This reaction concerns the decomposition of formic acid, and therefore is extremely interesting to an organic chemist. It is theoretically possible for this species to decompose into hydrogen gas and carbon dioxide, or into water and carbon monoxide. Thermodynamically, the decomposition into hydrogen gas and carbon dioxide is favored, but in concentrated acid the other pathway prevails. Morgan first reported this when observing an oscillatory evolution of gas over 80 years ago. Iron plays an important role in this reaction, as seen in the mechanism. An equilibrium exists between certain species, such as H_2O^+ and OH or $\text{H}(\text{CO})\text{OH}$ and $\text{H}(\text{CO})\text{OH}_2^+$, that is not shown in this mechanism.



The overall mechanism is simply shown as



Overall, these oscillating reactions represent an interesting, challenging, and diverse area of chemical research.

In this experiment, there were several sources that lead to the uncertainty seen in the results above. These sources of error were both random and systematic in nature. One source of random error may have been a nonhomogeneous reaction mixture, which is the reason stirring is completely necessary. The stir bar itself may have caused random error as it was seen to interfere with the laser beam at times. Bubbles of carbon dioxide may also have scattered the laser beam and caused random errors. Drifts of the laser or detector may have caused error. Interference from ambient lighting in the lab may have caused random errors. Finally, reflective losses as the laser is partially reflected from the reaction vessel may cause random deviations from the accepted period.

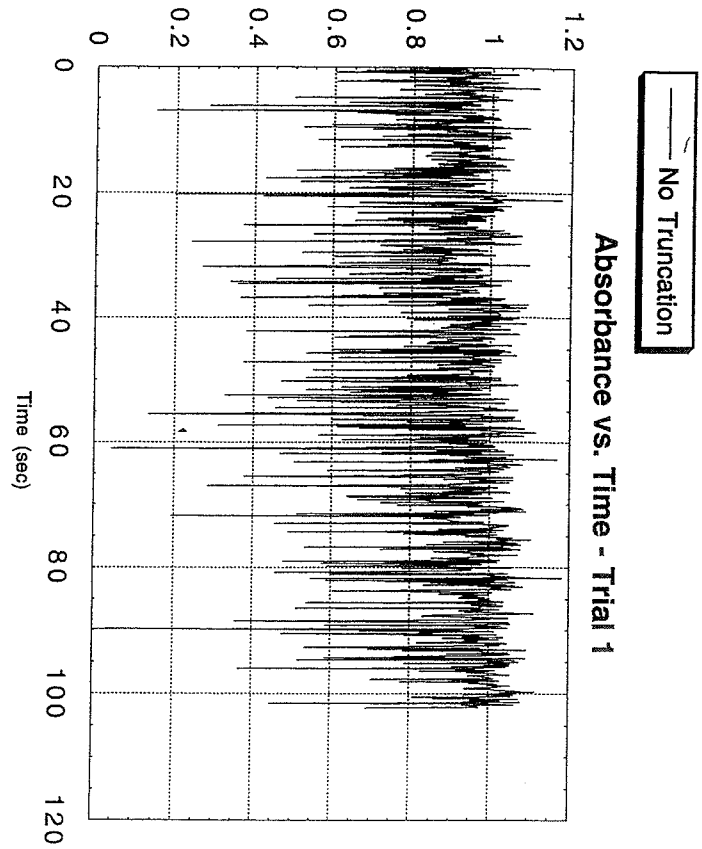
Systematic error may also have effected the results. If readings were not taken at the proper time intervals, the results would have deviated from the accepted values. If the chemicals that were used were old and impure, the period of the reaction could be effected. Along these lines, pieces of iron oxide could be seen in the feroin indicator. This could affect absorbance or the reaction itself. If refractive losses or carbon dioxide bubbles scattered the laser in a specific manner that is consistent throughout the experiment, systematic error may have resulted.

The plots of ReFFT versus frequency were difficult to interpret. Possible reasons for this complication include the fact that small deviations become a great deal larger upon inversion. Also, not all noise was necessarily of low frequency. There may be peaks which in fact correspond to noise in the same region of the spectrum as the BZ oscillation peaks. The intensity of the desired frequency peaks was not great and thus could be easily confused with noise. Additionally, it can be seen that because of the method used to obtain data, there are not a vast amount of possible values for period using this method of calculation. The repetitive values seen in the table illustrate this. Thus, even a period value of 102 seconds obtained using this method of calculation is not unreasonable. Finally, each plot has a noticeably high intensity peak at a frequency of zero. This is clearly not a possible signal and may have been caused by an error in the "Newerfourier" computer program. This intense peak may be interfering with desired signals and making data interpretation more difficult.

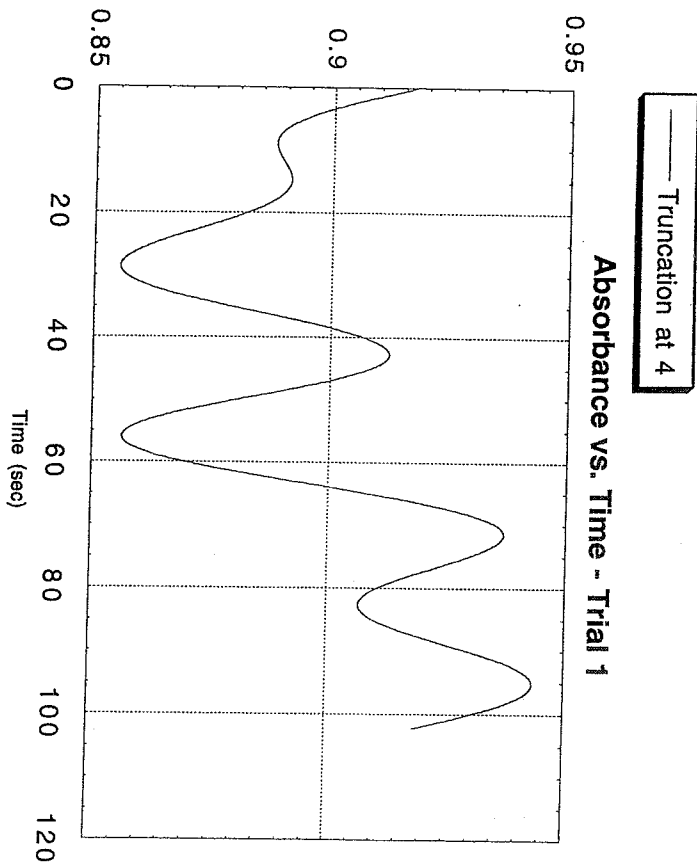
Overall, the results of this experiment were acceptable. The range obtained for the period of oscillation was $25 (\pm 7)$ seconds. Eastman, *et al.* reports a frequency of 30 mHz, which corresponds to a period of approximately 33 seconds. Extrapolating from Figure 4 in this publication also gives a period of approximately 33 seconds. While this is one second outside the given range, the deviation is not extreme and can most likely be attributed to systematic sources of error mentioned above. In addition, the range given is a 95% confidence interval. A 99% confidence interval would give a value of $25 (\pm 11)$ seconds, which would include the reported value. This experiment may be improved through collection of additional data points with a decreased time interval between readings, which would facilitate data interpretation, namely observation of frequency, a great deal. Overall however, this experiment served as an interesting and educational introduction to both oscillating chemical reactions and Fourier transforms.

→ deviation from Eastman *et al* could also be due to different temperature at which the rxn was run. (~~temp~~ rate of rxn. is highly dependent on temp.)

Absorbance



Absorbance



Truncation at 4 Truncation at 16 Truncation at 64
 Truncation at 8 Truncation at 32 Truncation at 128

Absorbance vs. Time - Trial 1

*arbitrary
 axes scale
 counter*

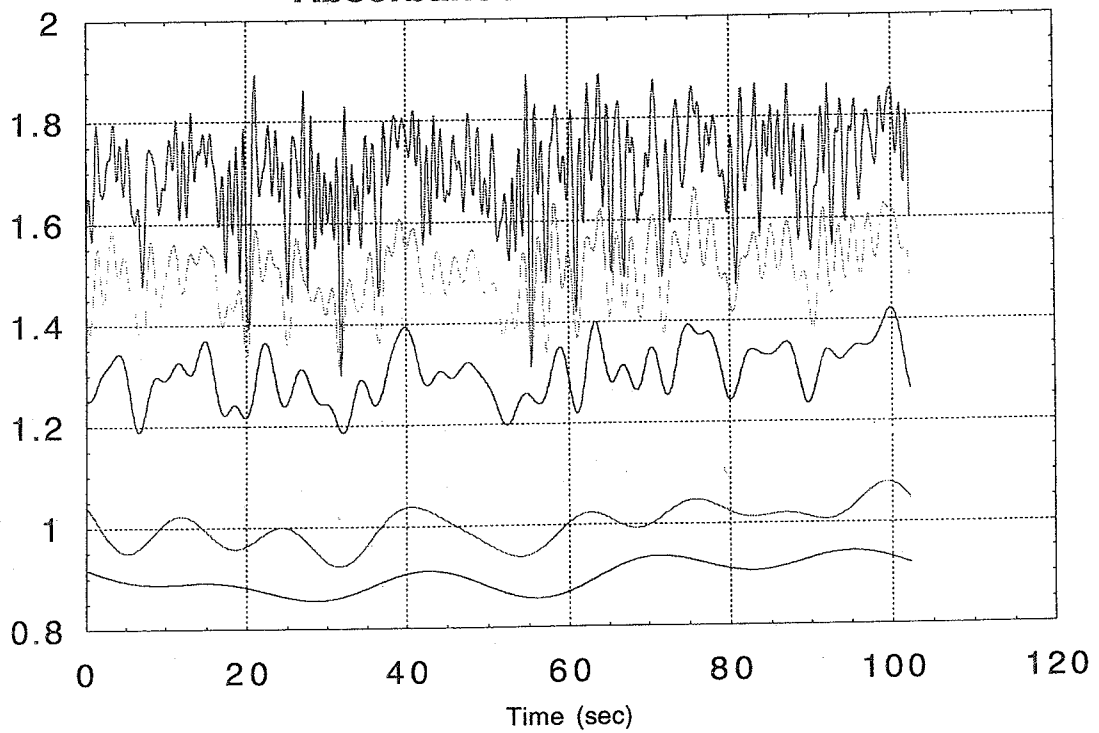


Figure I

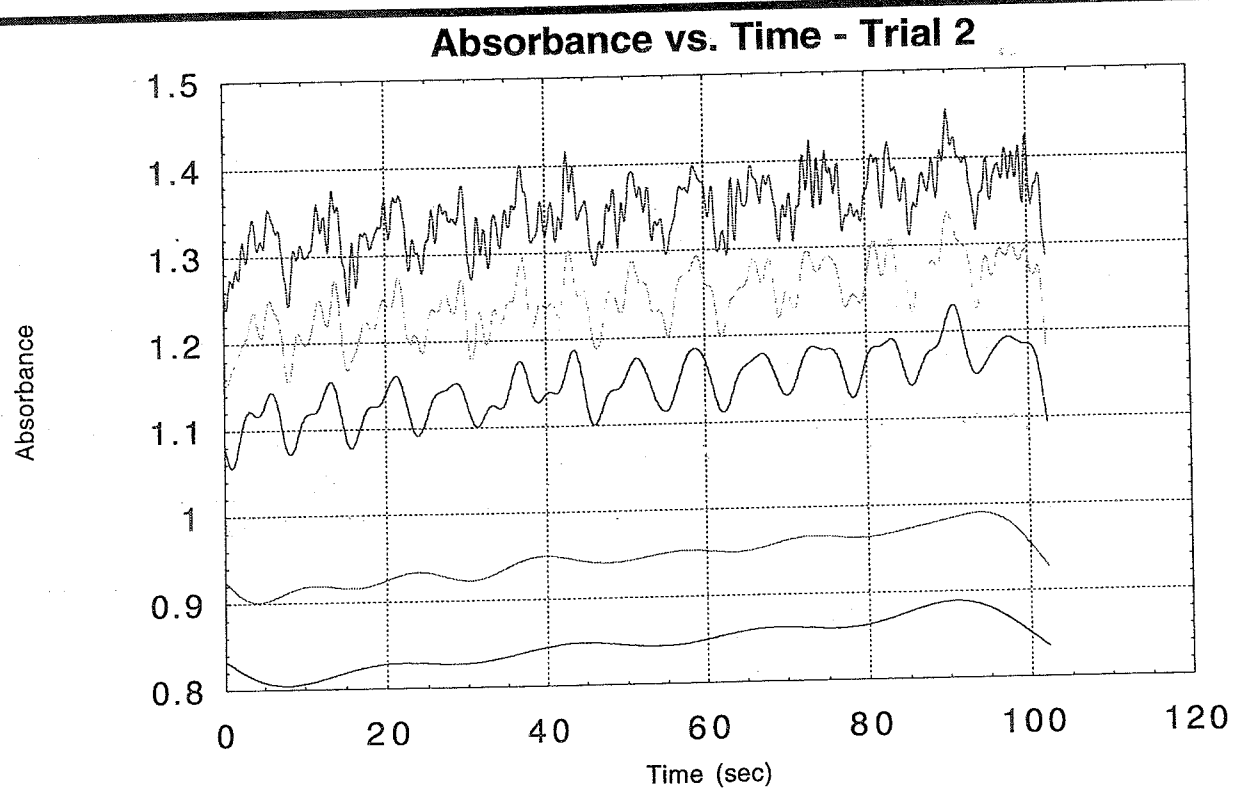
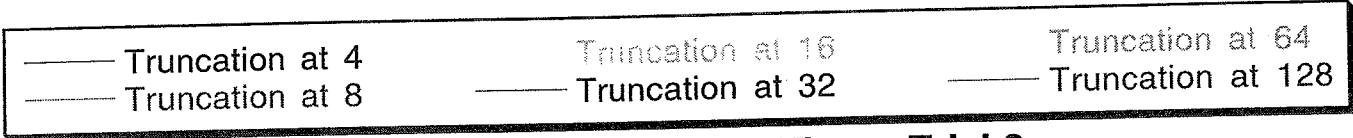
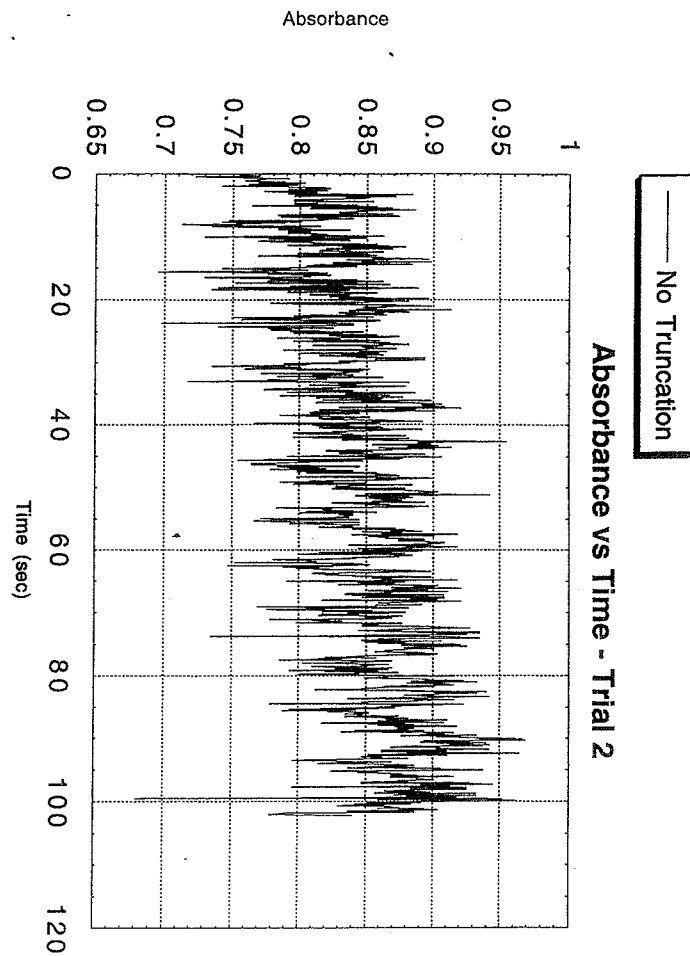
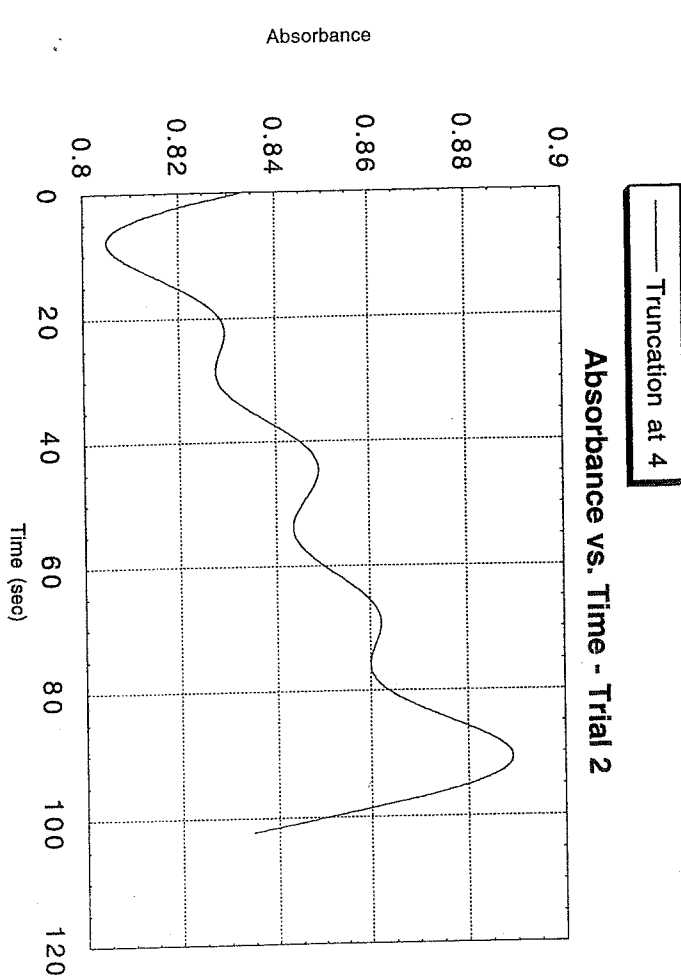
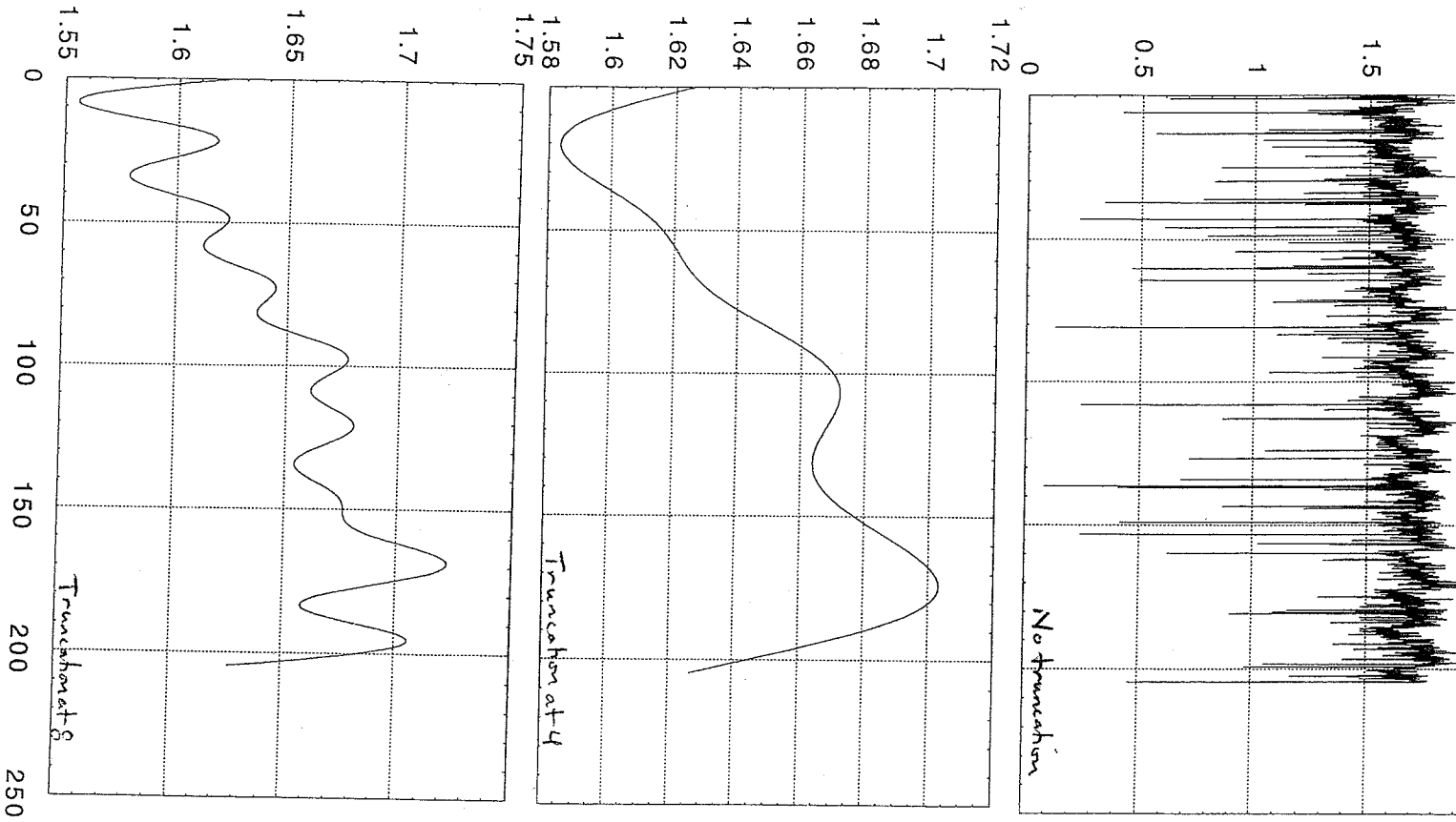


Figure II

Absorbance

Absorbance

Absorbance



Absorbance vs. Time - Trial 5

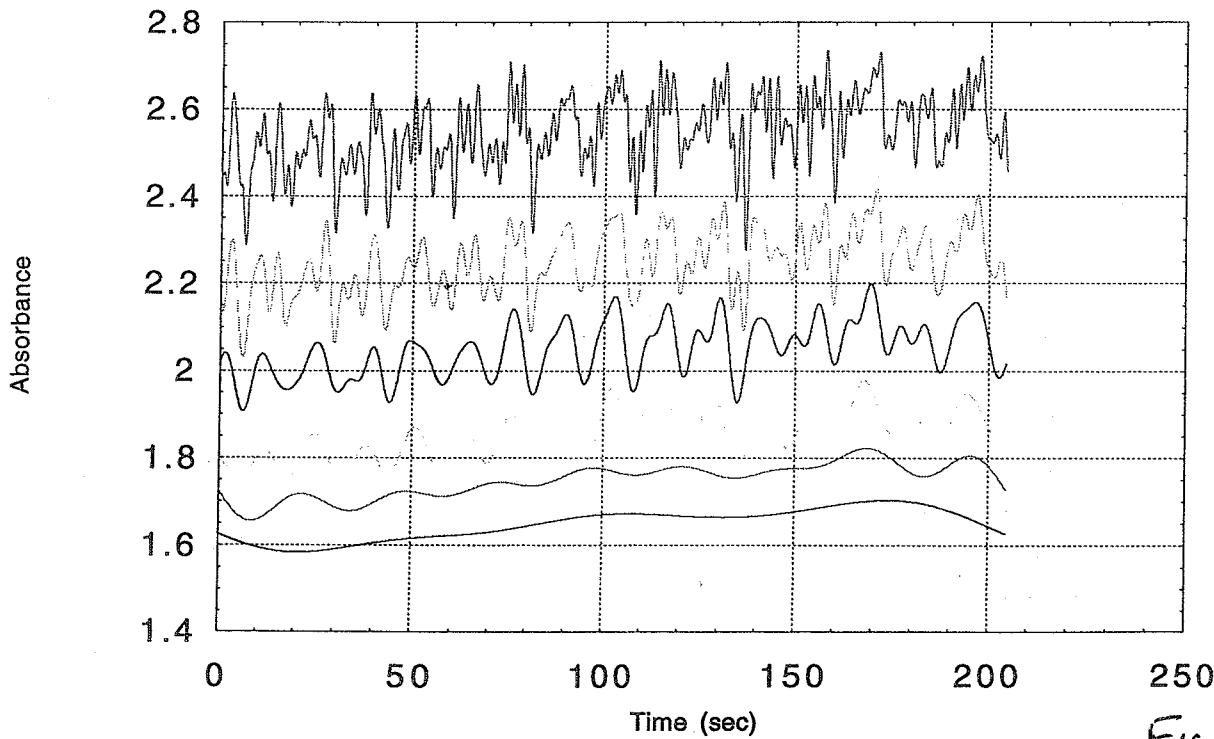


Figure III

— ReFFT

ReFFT vs. Frequency - Trial 1

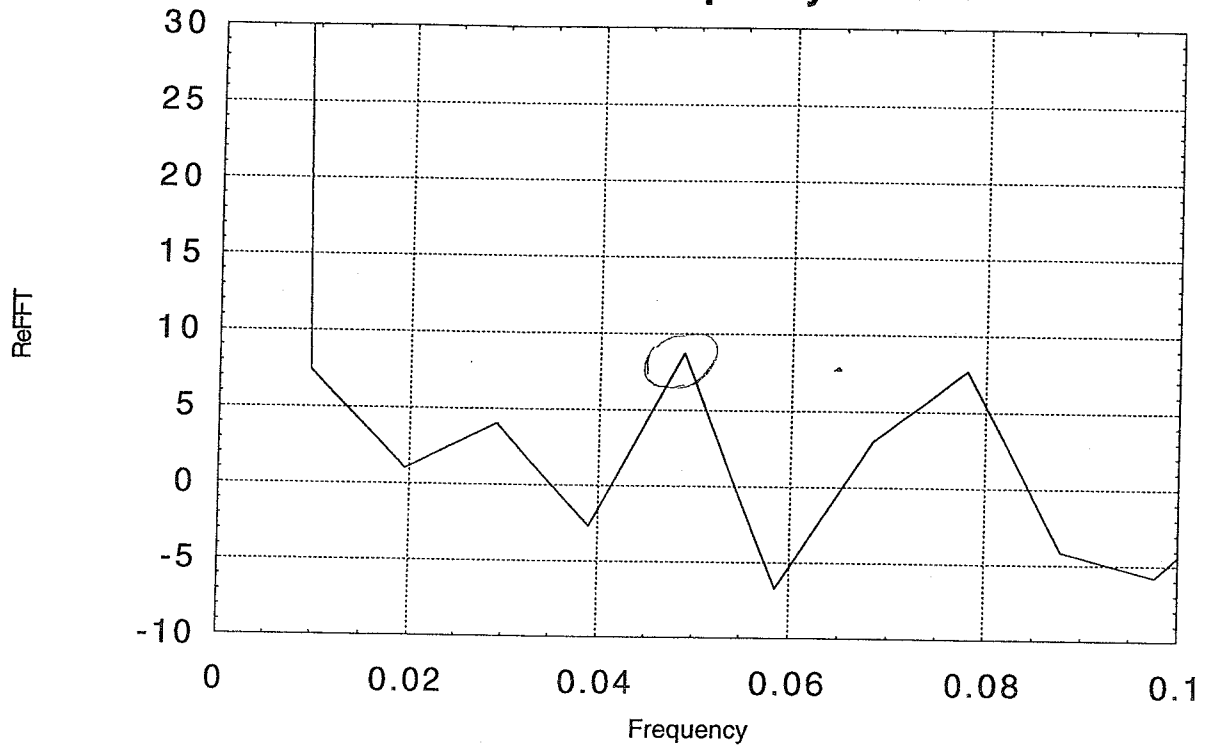


Figure IV

— ReFFT

ReFFT vs. Frequency - Trial 2

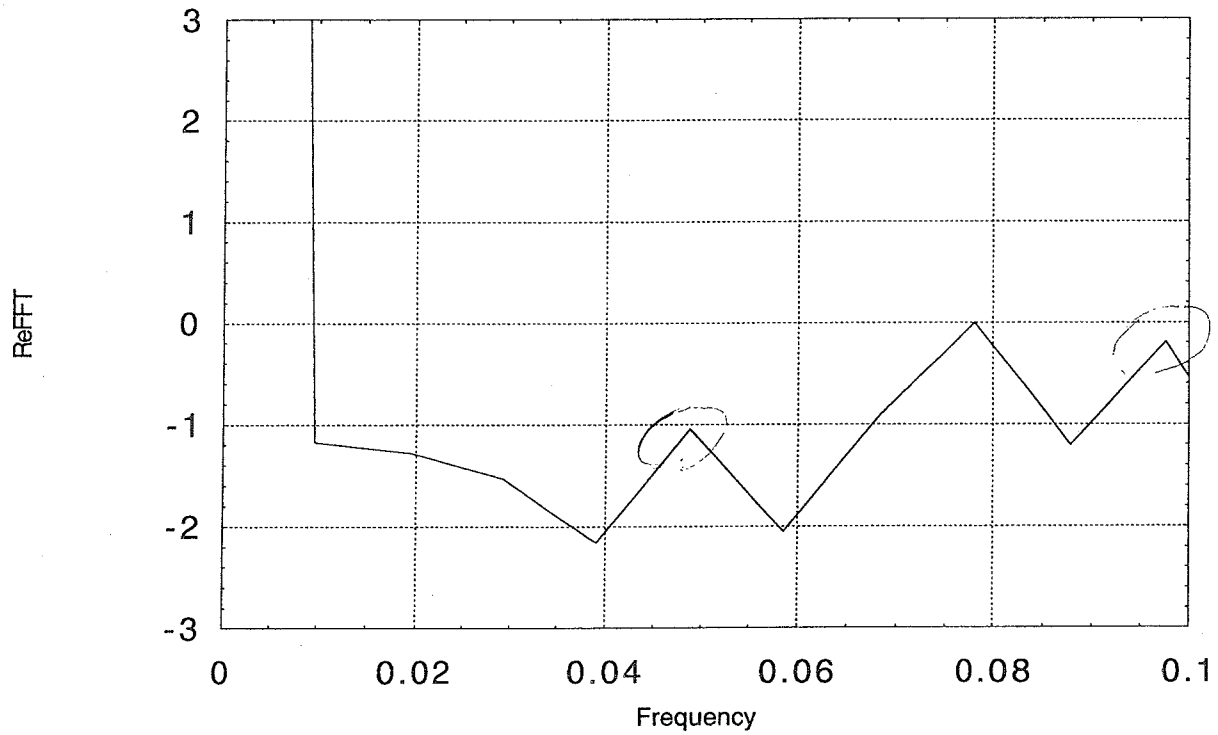


Figure V

— ReFFT

ReFFT vs. Frequency - Trial 3

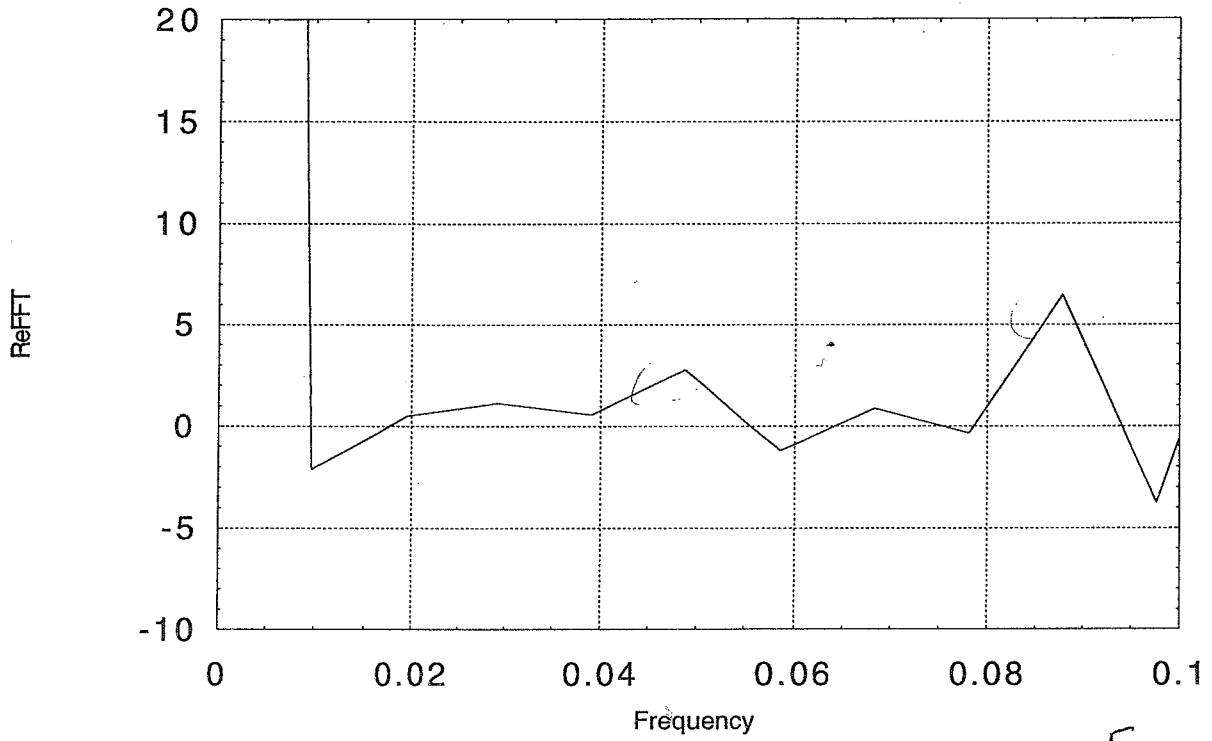


Figure VI

— ReFFT

ReFFT vs. Frequency - Trial 5

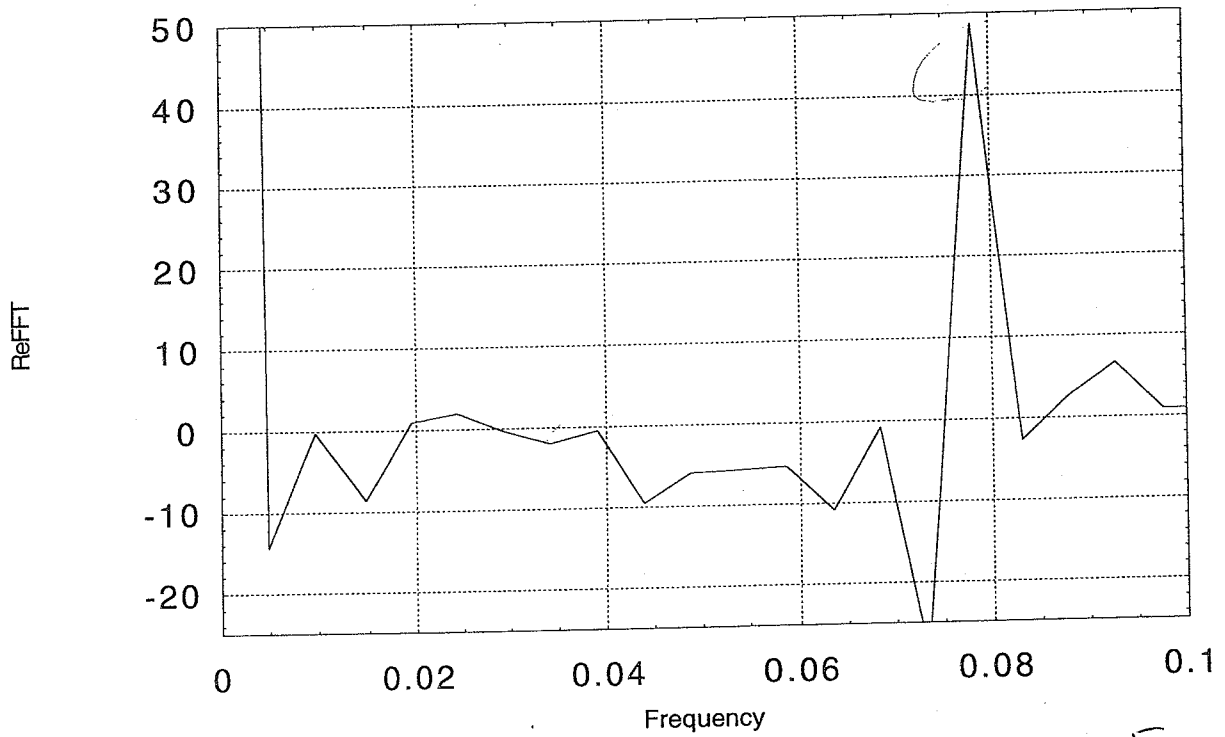


Figure VII