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DEVELOPMENT OF AN X-RAY FLUORESCENCE
SPECTROMETER WITH PEAK SEPARATION SOFTWARE
FOR IMPROVED RESOLUTION

by

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CHAPTER I

INTRODUCTION

This report describes the development of a microcomputer controlled X-ray fluorescence (XRF) spectrometer designed for use in a chemical processing plant. Both laboratory and on-stream applications are envisioned. The instrument is designed to be used in the dedicated quantitative analysis of a small number of predetermined elements.

Although significant improvements in XRF instrumentation have been made in recent years, especially in high resolution detector technology [1], many of these advances could not be applied because of cost, size and environmental restrictions. A major part of this report describes a computational method which permits the accurate determination of the areas of low resolution, possibly superimposed, XRF spectrum peaks.

An introduction to XRF, including the basic physics, detectors and electronic instrumentation, is presented in Chapter II. A design overview of the instrumentation under development is given in Chapter III and an algorithm useful in calculating the areas under overlapped peaks (such as XRF energy spectra) is described in Chapter IV. In addition to the algorithm definition, several examples are given to demonstrate its operation on computer synthesized data. The application of the technique to actual XRF data is presented in Chapter V. Some special requirements for XRF are also described and results are given.

CHAPTER II

X-RAY FLUORESCENCE PRINCIPLES AND TECHNIQUES

X-Ray Fluorescence Physics

X-ray fluorescence (XRF) is based on the emission of characteristic X-rays from excited atoms. A sufficiently energetic excitation source causes inner shell electrons to be ejected from an atom. The excited atom then returns to a lower energy state when an outer shell electron falls back to a lower energy level, with the energy difference being given off in the form of a fluorescent X-ray. The nomenclature used to describe some of the different energy transitions is given in Figure 1.

Actually this representation is somewhat simplified in that a certain amount of splitting of these energy levels occurs due to variations in the total electron angular momentum of an atom [2]. As a result, more than one fluorescent X-ray energy for each transition can be observed with sufficiently high resolution equipment. The amount of splitting is small, especially with the low atomic number elements. As an example, the energies for the calcium $K\alpha$ transition are $K\alpha_1 = 3.688$ KeV, $K\alpha_2 = 3.692$ KeV [3].

In order for fluorescence to occur, the atom must be raised from its ground state energy to an excited state. The excitation source can be an X-ray of higher energy than the fluorescent X-ray to be observed. A radioactive isotopic element which produces X-ray radiation is a convenient and commonly used source of these exciter X-rays.

The number of fluorescent X-rays of a particular energy emitted from an irradiated sample is directly proportional to the number of atoms (or concentration) of the corresponding element in the sample. Unfortunately,

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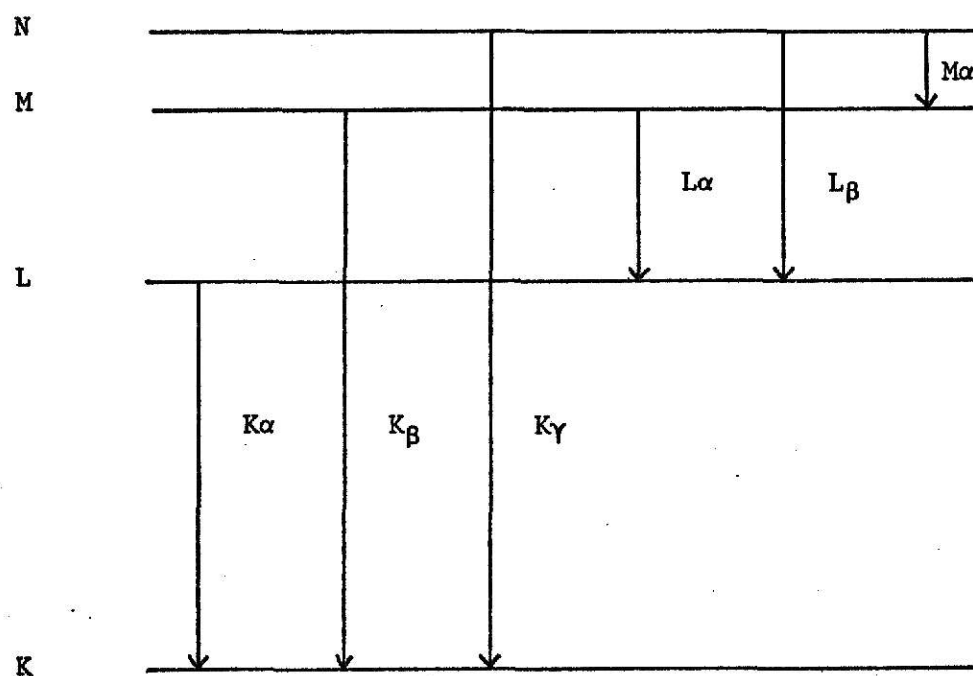


FIGURE 1: X-Ray Transitions

the fluorescent X-ray energy lines are spread out by some of the common detectors, resulting in a broad energy peak instead of a narrow line. The problem then becomes one of determining the area under the broadened peak.

Detectors

Several types of detectors can be used to monitor the fluorescent X-rays [4]. The detectors commonly used can be categorized as:

1. gas filled detectors
2. scintillation detectors
3. solid state detectors

The gas filled detector is basically a metal chamber, filled with a suitable gas, which contains a positively biased (with respect to the shell) anode wire. An X-ray passing through the gas produces free electrons and positive ions. The free electrons are accelerated toward the anode at energies high enough to ionize other atoms resulting in an electron flow which can be detected. Over a fairly wide anode voltage range, which depends on the detector geometry and gas pressure, the anode current pulses are proportional to the original X-ray energy.

Scintillation detectors are based on materials which emit a pulse of light when an X-ray passes through them. The light pulses are detected with a photomultiplier tube. Various types of scintillation materials are available such as CsI and NaI solid crystals and plastic scintillators which usually contain anthracene as the active component. Unfortunately, the solid crystal detectors are very susceptible to fracture by thermal gradients and the plastic scintillators suffer from poor resolution.

A solid state detector is basically a p-i-n diode of extremely large dimensions - ≈ 1 cm intrinsic region. Although these detectors offer very

good resolution and sensitivity, liquid nitrogen temperatures are required. Cooling must be maintained even during transportation and storage of the device. These requirements limit its usefulness except in high resolution laboratory type equipment.

Because of these reasons, the instrument under development will use a gas filled proportional detector. The physical layout of the source, detector and sample is shown in Figure 2.

Instrumentation

The basic instrumentation for X-ray fluorescence is given in Figure 3. A simplified detector and preamp functional circuit is shown in Figure 4. Assuming an ideal amplifier with gain A, the transfer function is:

$$V_o = \frac{I_d}{(1 + \frac{1}{A})(sC_f) + (\frac{1}{A}) sC_d} \quad (1)$$

For $A \gg 1$ and $AC_f \gg C_d$, this reduces to:

$$V_o = \frac{I_d}{sC_f}$$

or

$$v_o(t) = \frac{1}{C_f} \int i_d dt = \frac{Q_d}{C_f} \quad (2)$$

A typical value for C_f is 1 pF, yielding $v_o = 10^{12}$ Q. The output pulse rise time is on the order of 40-100 ns and the fall time, which depends on an RC time constant in the preamp, is ≈ 50 -100 μ sec. The main amplifier provides additional voltage gain in addition to its function of pulse shaping to reduce the length of the pulse tail. The amplifier voltage gain is typically in the range of 100-1000.

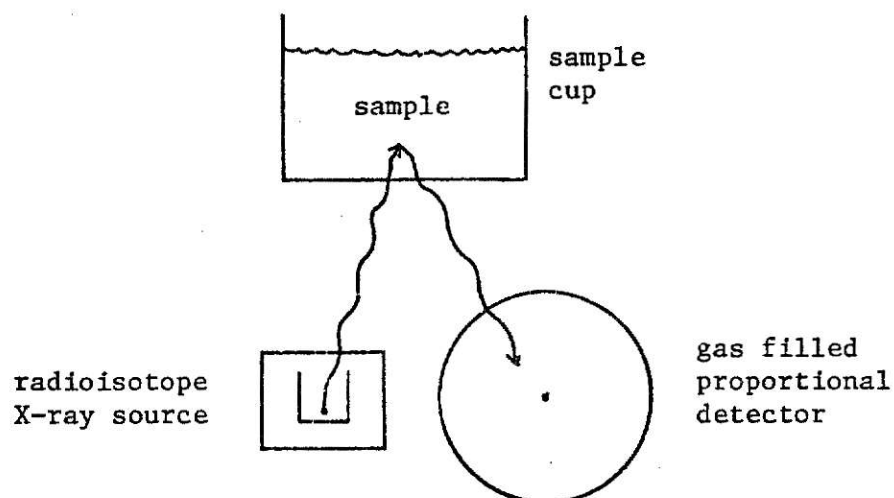


FIGURE 2: Detector Geometry

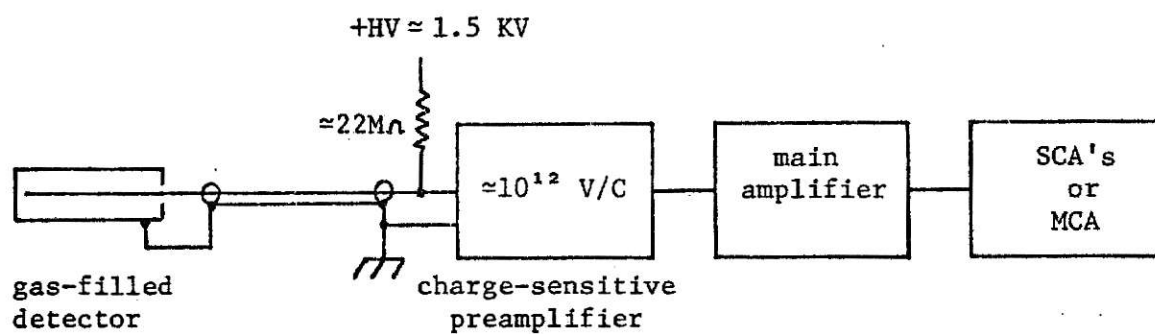


FIGURE 3: X-Ray Fluorescence Instrumentation

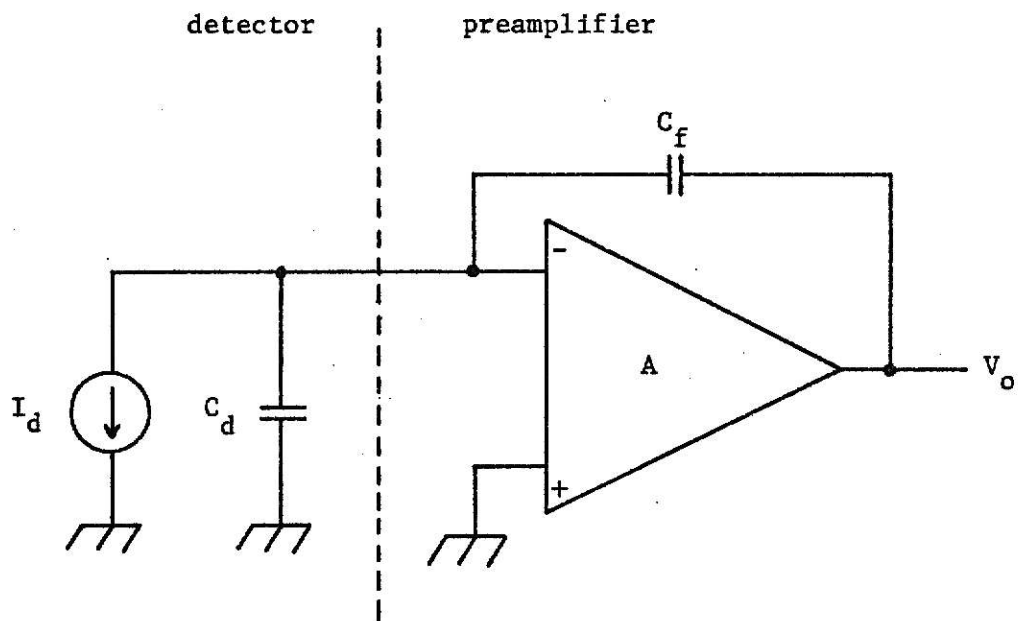


FIGURE 4: Detector and Preamplifier Model

The output of the amplifier is then a series of voltage pulses with height proportional to the original incident X-ray energy. The number of pulses of a given voltage level is related to the concentration of the sample element which produced those pulses. For quantitative analysis one has to measure the number of pulses in this energy range.

Single Channel Analysis

A simple way to determine the number of pulses within an energy range is to use two comparators with the thresholds set just above and below the region of interest along with the circuitry to detect when the pulse voltage is between the two levels as shown in Figure 5 [5].

Various types of coincidence logic are used. This counting method, using what is referred to as a single channel analyzer (SCA), is not adequate in many applications for several reasons. Some type of automatic gain control is often required, usually based on a second SCA which holds the pulses of an internal standard at a fixed voltage level [6]. The presence of overlapped fluorescence peaks causes computational difficulties.

Multichannel Analysis

An alternate analysis method involves the use of a multichannel analyzer (MCA) [7]. In this method, a fast analog-to-digital converter (A/D) with sample and hold (S/H) and peak detection circuitry is used to digitize the pulse heights as shown in Figure 6. The resolution of the A/D is typically 8-14 bits, with high resolution detectors requiring a higher resolution A/D. The digital value of the pulse height is then used as a memory address for an increment memory circuit. This results in an X-ray spectrum of counts (number of pulses) vs. voltage (X-ray energy) where the quantized voltage is

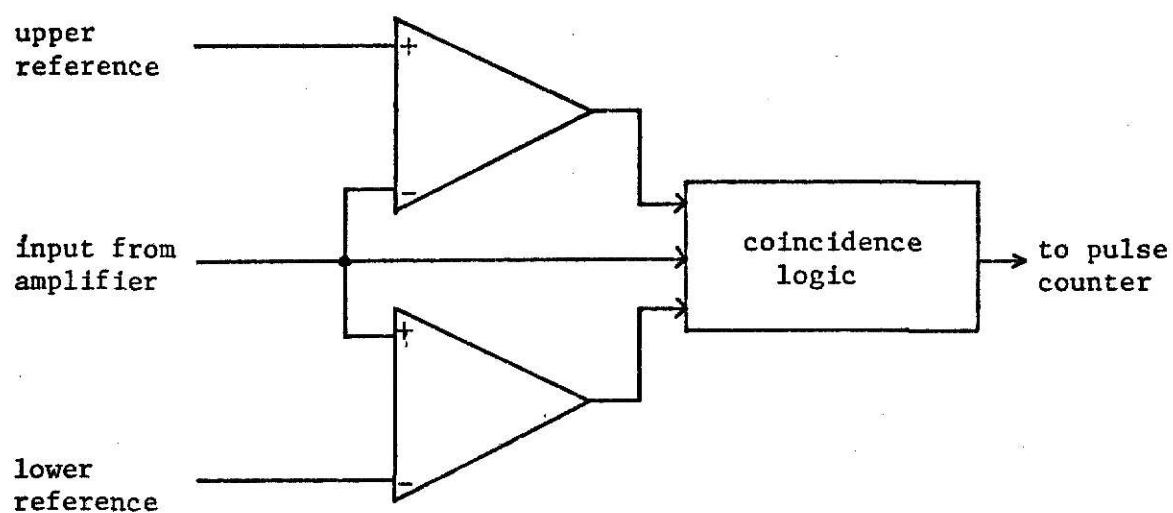


FIGURE 5: Single Channel Analyzer

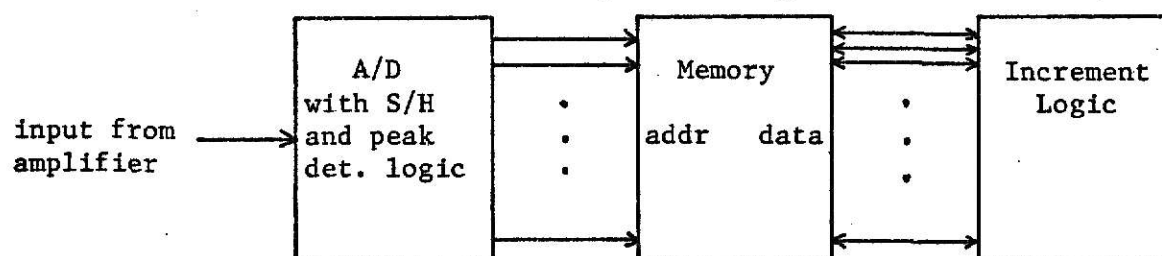


FIGURE 6: Multichannel Analyzer

commonly referred to as the "channel number". A typical spectrum is shown in Figure 7.

Analog-to-Digital Converters

Two types of A/D's are commonly used in nuclear instrumentation [7]:

1. counter or single-slope
2. successive approximation

In the single-slope type, the peak pulse amplitude is held on a capacitor which is then discharged to zero voltage by a constant current source. The discharge time is measured by a gated counter. For an 8 bit converter, the maximum conversion time is $256t$ where t is the period of the counter clock. For a 50 MHz clock, the maximum conversion time is $\approx 5.1 \mu\text{sec}$. It is noted that the conversion time varies directly with the pulse height.

In the successive approximation A/D, the input voltage is first compared with $V_{fs}/2$ where V_{fs} is the full scale A/D range. The most significant (MS) bit is then set or cleared depending on the outcome of this comparison. The input voltage is then compared to the results of the previous conversion plus $V_{fs}/4$ and the next bit is set or cleared, etc. Thus only N comparisons are required rather than the 2^N for the single slope A/D. In addition to the speed advantage, the successive approximation A/D is readily available in a small IC type package.

An important specification of an A/D to be used in spectrum analysis is the differential nonlinearity. This is the deviation between the measured step width and the ideal width. For example, assume an 8 bit A/D with a differential nonlinearity of $\pm \frac{1}{4}$ LS bit as shown in Figure 8.

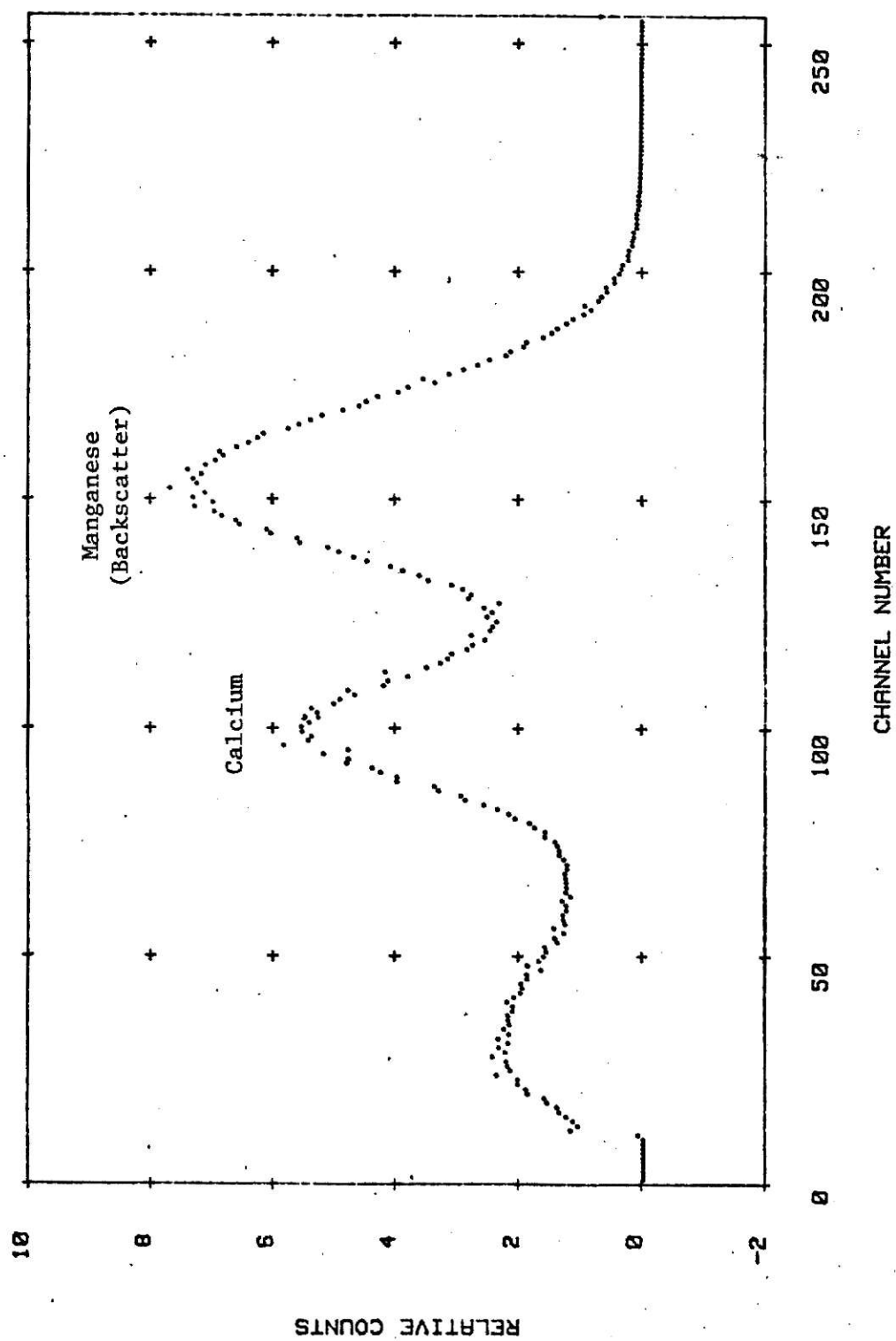


FIGURE 7: Calcium XRF Spectrum

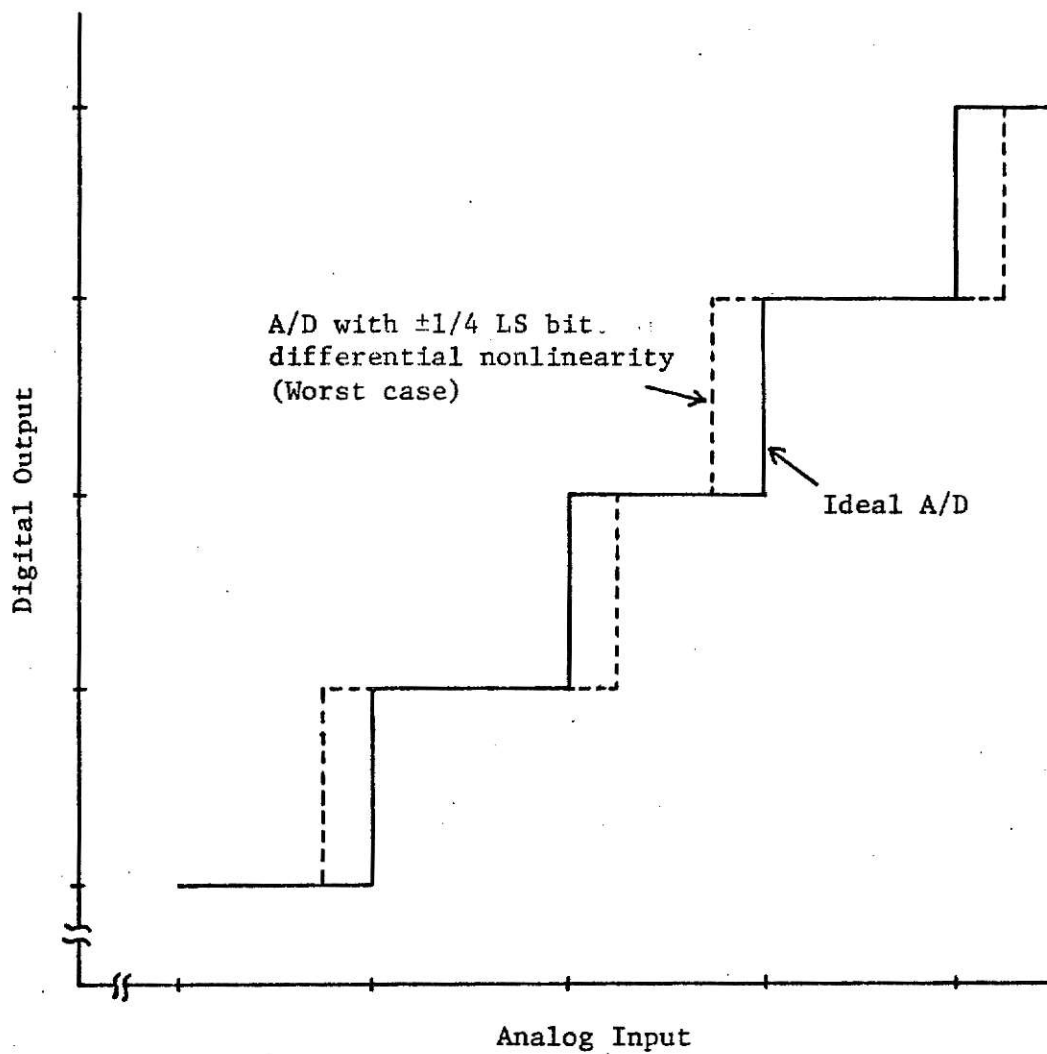


FIGURE 8: Analog-to-Digital Converter Differential Nonlinearity

A worst case spectrum taken with such an A/D would have 50% too many counts in every other channel and 50% too few counts in the remaining channels, or an error of $\pm 50\%$. A similar analysis on A/D's with other differential nonlinearity (DNL) specifications can be used to obtain the following relation for worst case error:

$$\text{error (\%)} = \pm 2 \cdot \text{DNL} \cdot 100 \quad (3)$$

It is noted that in order to realize a worst case error of $\pm 3\%$ with an 8 bit converter, a differential nonlinearity of $\pm 1/64$ bits is required. This corresponds to a 13 bit A/D with $\pm 1/2$ bit worst case differential nonlinearity, which is about the state of the art for A/D converters with the desired conversion time of 2-5 μsec . Such an A/D, short-cycled to 8 bits, was used to obtain the data presented in Chapter V of this report.

CHAPTER III

XRF INSTRUMENT HARDWARE

The actual hardware for the instrument under development will now be described in somewhat general terms. Since suitable detectors, preamps, and main amplifiers are available commercially, these components will not be discussed here. The remaining electronic hardware can be functionally separated into two parts:

1. The spectrum analyzer which consists of the A/D converter, the increment memory hardware and other associated hardware (i.e. an MCA).
2. The main computer for performing the computational algorithm to calculate the desired data and to provide operator interfacing via keyboard and display.

A block diagram of the spectrum analyzer section is given in Figure 9.

The FIFO (first in-first out) buffer permits the short term acquisition rate to be dependent on the A/D rather than the increment memory circuitry. This allows the use of a microcomputer to perform the increment memory operation, simplifying the component count and circuit complexity. Although a separate dedicated microcomputer is not strictly required, it frees the main processor during spectrum acquisition for other functions such as updating displays on operator request, etc. The data memory is electronically organized as 512 8-bit bytes. Functionally however, it provides 256 16-bit words which allows a maximum of $2^{16} - 1$ or 65535 counts in each of the 256 channels. The high speed 8085A-2 microprocessor has a clock cycle time of 200 ns, which yields an increment memory

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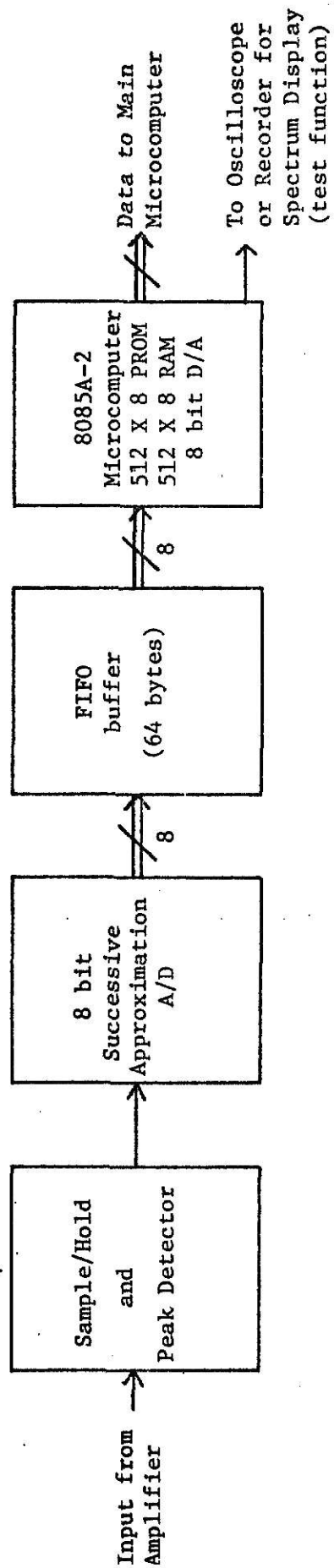


FIGURE 9: Spectrum Analyzer Block Diagram

time of 13 μ sec. for the LS byte. An additional 5 μ sec. is required for the MS byte on the 256th increment of a particular channel. The 8085 assembly language mnemonics for the interrupt initiated 16 bit increment memory function are given below:

```

INT:  IN    ADC      ;START OF INTERRUPT, READ A/D
      MOV    L,A     ;SET UP MEMORY POINTER
      INR    M       ;INCREMENT LS BYTE
      INX    SP      ;RESTORE STACK POINTER TO VALUE
      INX    SP      ; BEFORE INTERRUPT CALL
      JZ     HIBYTE  ;OVERFLOW?
      EI     ;ENABLE INTERRUPTS
      HLT      ;AND WAIT FOR NEXT PULSE

HIBYTE: INR    H      ;POINT TO MS BYTE
      INR    M       ;INCREMENT MS BYTE
      JZ     DONE    ;OVERFLOW?
      DCR    H       ;RETURN POINTER TO LS BYTE
      EI     ;ENABLE INTERRUPTS
      HLT      ;AND WAIT

```

When a complete spectrum has been acquired, it is transferred to the main microprocessor via I/O ports. After the transfer is complete, the spectrum analyzer can start acquiring a new spectrum while the previous spectrum is evaluated by the main computer.

The main computer section of the instrument, shown in Figure 10, consists of a standard Intel 8085A microprocessor, EPROM for instruction storage, and RAM for temporary data storage. The computer program is written in Intel's PLM high level language. The floating point math hardware increases the execution speed of the math calculations by about an order of magnitude. The computational algorithms are the subject of the next two chapters of this report.

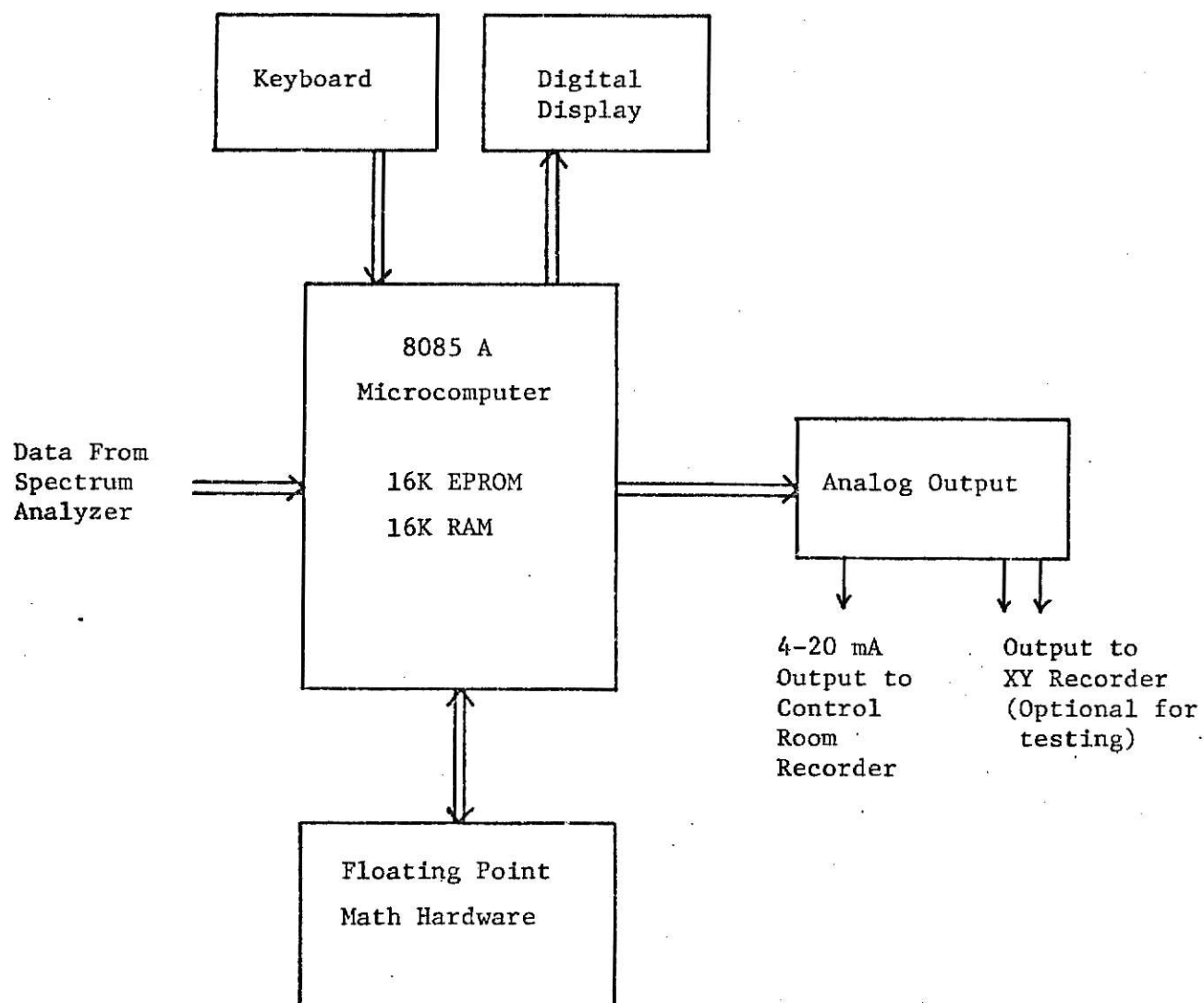


FIGURE 10: Main Computer Block Diagram

CHAPTER IV

PEAK SEPARATION ALGORITHM

Ideally, all that is required in calculating elemental concentration from an XRF spectrum is to determine the number of counts in the photopeak and multiply by a scaling factor. In actual practice, however, things are much more complicated. Corrections must be made for dead time in the amplifier and A/D system, caused by overlapped fluorescence pulses. In addition, one has to consider source decay when using a radioisotope source. These two problems can be solved by ratioing the photopeak to the backscatter (BKS) peak (discussed in Chapter V). Another problem is the background which causes the calibration curve to pass through some point other than zero. The problem of overlapped peaks, however, was probably the most difficult to surmount.

It was learned that Dow Chemical had purchased a peak separation program from Surface Science Labs of Palo Alto, CA for use on ESCA (Electron Spectroscopy for Chemical Analysis) spectrometer data. Unfortunately, very little written documentation existed for the program. Through considerable effort, a flow chart was developed and an understanding of the algorithm was obtained. In this chapter the algorithm will be discussed.

Peak Parameters

The algorithm is an iterative method where initial estimates of peak parameters are modified so as to more closely approximate the original data. The peak parameters as shown in Figure 11 are:

1. position—channel number
2. height—number of counts at the peak center
3. width—number of channels in peak, measured at $\frac{1}{2}$ peak height

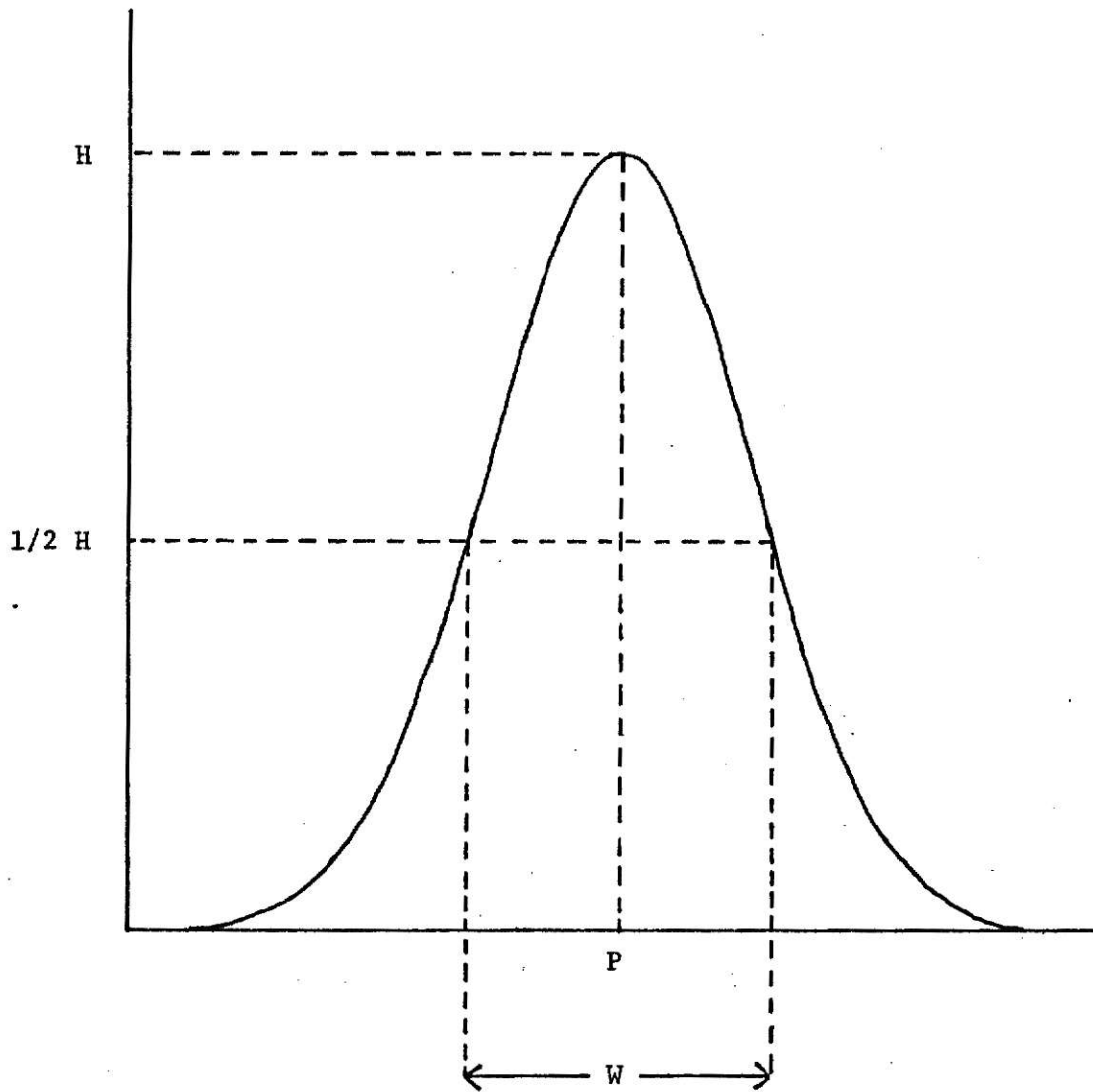


FIGURE 11: Peak Parameters

Initial parameter estimates can be obtained by a visual inspection of the data or a relatively simple computer algorithm can be used.

Peak Images

Although the peaks may have arbitrary shapes, Gaussian shapes will be assumed for this initial discussion. The peak shapes are defined by a discrete image array, G , which contains the height of the image at equal position increments. An array of 256 points, $G(0)$ through $G(255)$, was chosen. (This is somewhat an arbitrary value and is probably excessive.) The image peak is centered in the array, at $G(128)$, and it should be normalized to have a maximum value of one. The Gaussian image was defined as:

$$G(I) = e^{\frac{-(I-128)^2}{500}} \quad 0 \leq I \leq 255 \quad (4)$$

Since each peak will be assumed to be Gaussian for the present discussion, each image G_j for each peak j will be defined as above.

The width at one-half maximum peak height of such an image can be calculated from the Gaussian p.d.f.:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (5)$$

with mean μ and variance σ^2 . At the maximum peak height,

$$f(\mu) = \frac{1}{\sigma\sqrt{2\pi}} \quad (6)$$

At one-half maximum height,

$$f(x) = \frac{1}{2\sigma\sqrt{2\pi}} = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (7)$$

Solving for X yields:

$$X = \mu \pm \sigma \sqrt{-2 \ln \frac{1}{2}} \quad (8)$$

The total peak width is then:

$$W_g = 2\sigma\sqrt{-2 \ln \frac{1}{2}} = 2.355\sigma \quad (9)$$

Then for the image defined above, with $\sigma = \sqrt{250}$,

$$W_g = 37.23 \quad (10)$$

Peak Estimate Error

An error array is calculated by adjusting the image shape for the parameter estimates, summing the contribution from each peak and finally subtracting the actual data.

The height of spectrum peak j at channel I is calculated from:

$$Y_j(I) = H_j G_j \left(\frac{W_{gj}}{W_j} \cdot (I - P_j) + 128 \right) \equiv H_j G_j(X) \quad (11)$$

where

G_j = image array, defined above

W_{gj} = width of image for peak j

P_j = position estimate for peak j

H_j = height estimate for peak j

W_j = width estimate for peak j

I = a channel within peak j

Since the value of X defined above can be noninteger, corresponding to some point between two discrete image points, the image value $G_j(X)$ is actually obtained by linear interpolation between the nearest two image points. Each image value $G_j(X)$ is then multiplied by the height estimate for peak j .

The contributions from each peak are then summed channel by channel, and finally each data point is subtracted channel by channel to obtain an error array:

$$E(I) = \left[\sum_{\substack{j = \text{all} \\ \text{peaks}}} Y_j(I) \right] - D(I) \quad 0 \leq I \leq 255 \quad (12)$$

where

$D(I)$ = spectrum data for channel I

Parameter Adjustment

The error array $E(I)$ is then multiplied by three functions for each peak. These functions are designed to distinguish between errors in position, height and width respectively. These functions or "filters" are defined below and a sketch of each is given in Figure 12.

$$F1_j(I) = (1 - \left| \frac{I - P_j}{W_j} \right|) \cdot \text{sign}(P_j - I) \quad P_j - W_j \leq I \leq P_j + W_j \quad (13)$$

$$F2_j(I) = (1 - \left| \frac{I - P_j}{W_j} \right|) \quad P_j - W_j \leq I \leq P_j + W_j \quad (14)$$

$$F3_j(I) = (1 - \left| \frac{I - P_j}{W_j} \right|) \cdot \text{sign}(0.2 - \left| \frac{I - P_j}{W_j} \right|) \quad P_j - W_j \leq I \leq P_j + W_j \quad (15)$$

Parameters adjustment terms are then calculated from:

$$P'_j = \frac{\sum_{I=P_j-W_j}^{P_j+W_j} F1_j(I) \cdot E(I)}{H_j} \quad (16)$$

$$H'_j = - \frac{\sum_{I=P_j-W_j}^{P_j+W_j} F2_j(I) \cdot E(I)}{W_j} \quad (17)$$

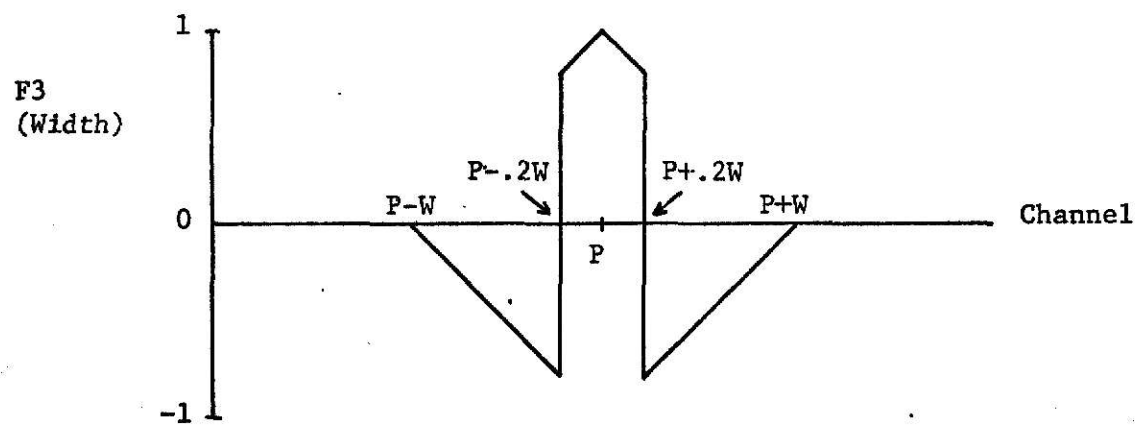
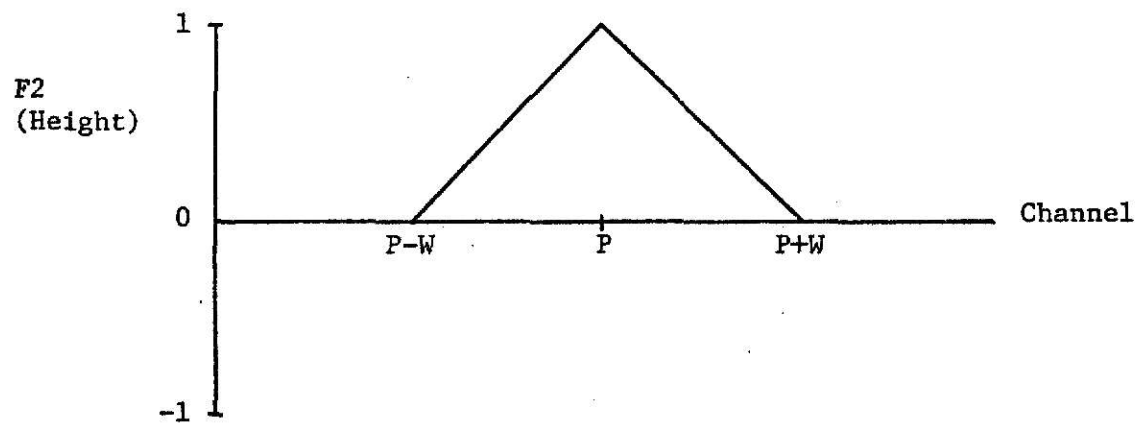
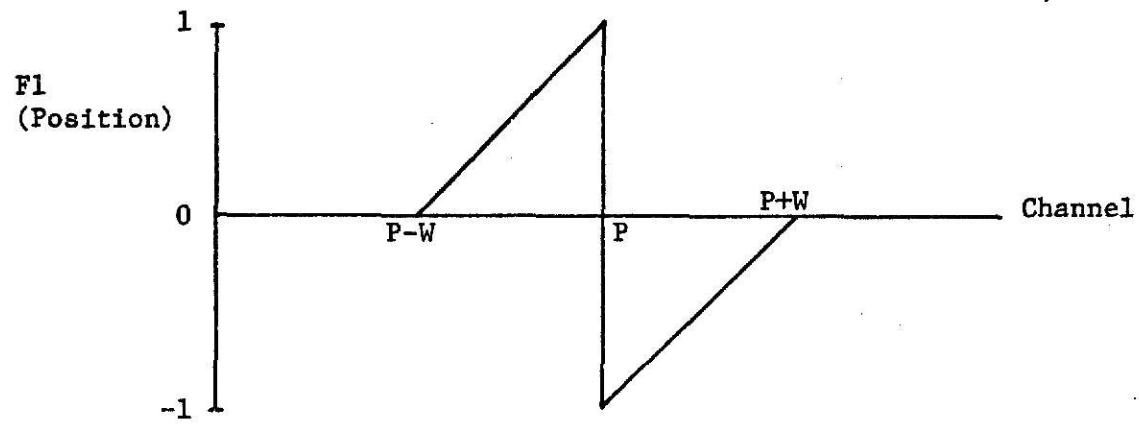


FIGURE 12: Parameter Adjustment Functions

$$W'_j = \frac{3}{2} \cdot \frac{\sum_{I=P_j-W_j}^{P_j+W_j} F3_j(I) \cdot E(I)}{H_j} \quad (18)$$

And finally the parameters are modified:

$$\begin{aligned} P_j &\leftarrow P_j + P'_j \\ H_j &\leftarrow H_j + H'_j \\ W_j &\leftarrow W_j + W'_j \end{aligned} \quad (19)$$

Filter F1 ("position filter") is a center weighted function which determines the difference between the error function to the left and to the right of peak center. The divisor H_j in the calculation of P'_j normalizes the peak height to 1 for the position adjustment term. Filter F2 ("height filter") weights the error function E near the center of the peak. The product of $F2 \cdot E$ gives the center weighted difference between the areas under the data peak and the peak estimate. The division by W_j yields a height adjustment term with units of height. Filter F3 ("width filter") gives opposite polarity weighting to the center of the peak error as the tails. The H_j division in the calculation of W'_j normalizes the height to 1 and the factor of $3/2$ is included to hasten convergence.

If the parameter estimates are extremely bad or if the height or width parameters are sufficiently small, the adjustment terms P'_j , H'_j and W'_j can become extremely large and the desired convergence may not be attained. Hence it may become necessary to limit the values of the adjustments. Different limits can be used depending on the application. The limits chosen for XRF data are:

$$\left| P'_j \right| < 3 \quad \left| H'_j \right| < 0.3 H_j \quad \left| W'_j \right| < 0.3 W_j \quad (20)$$

Usually the parameters can be estimated with sufficient accuracy that these limits are inoperative.

Operation on Synthesized Spectra

The following several pages show the operation of the algorithm for artificial computer generated data. Figure 13 demonstrates the position error results for a single Gaussian peak. The initial error array (estimate minus data) is shown in Figure 13c. The error array multiplied by filter F1 (Figure 13d) is shown in Figure 13e. The area under this curve is used in calculating the position adjustment. Similar data for filter F2 and F3 are shown in Figure 13f through 13i. The peak estimate after 1 iteration is given in Figure 13j. The error array after the first iteration is shown in Figure 13k and after the 2nd and 7th iteration in Figure 13l. The final peak estimate (7 iterations) is given in Figure 13m. The percent relative standard error given on the computer printout in Figure 13a is calculated as the RMS error divided by the average height:

$$\text{Rel. Std. Error (\%)} = \frac{\sqrt{\frac{\sum_{I=0}^{255} [E(I)]^2}{256}}}{\frac{\sum_{I=0}^{255} D(I)}{256}} \times 100 \quad (21)$$

Figure 14 shows similar results for operation on a single peak with a height error and Figure 15 for a width error.

Separation of two overlapped Gaussian peaks is shown in Figure 16. An artificially generated spectrum and a starting estimate are shown in Figure 16b. The initial error curve and the error curve after 1 iteration are given in Figure 16c, the error after 7 iterations is given in Figure 16d

All of the preceeding artificial peaks were ideal data—no noise. Figure 17 shows the peak separation on the same data as the previous set, except that a pseudo random noise with a peak to peak amplitude equal to $\frac{1}{2}$ of the height of the small peak has been added. The raw data and initial estimate curves are shown in Figure 17b and 17c respectively. The initial error is plotted in Figure 17d, the error after 7 iterations in 17e, and the resultant individual peaks and peak sum are given in Figure 17f.

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AVAILABLE.**

SP01, ARTIFICIAL GAUSSIAN SPECTRUM

P1= 100.0000

H1= 800.0000

W1= 50.00000

P-P NOISE= 0.000000

PLOTTER SCALE FACTOR (COUNTS/DIV): 100

IMG1, NORMALIZED GAUSSIAN IMAGE

AREA = 42578.63

PASS # 0 REL STD ERROR (%) = 116.2996

P 1= 120.0000

H 1= 800.0000

W 1= 50.00000

A 1= 42578.74

PASS # 1 REL STD ERROR (%) = 36.84240

P 1= 105.3320

H 1= 691.4305

W 1= 58.10053

A 1= 42767.77

PASS # 2 REL STD ERROR (%) = 17.29048

P 1= 98.94327

H 1= 716.0479

W 1= 54.20691

A 1= 41377.63

PASS # 3 REL STD ERROR (%) = 9.853540

P 1= 100.4839

H 1= 750.6508

W 1= 52.13369

A 1= 41656.95

PASS # 4 REL STD ERROR (%) = 5.166656

P 1= 100.1010

H 1= 773.1578

W 1= 51.16768

A 1= 42110.95

PASS # 5 REL STD ERROR (%) = 2.819331

P 1= 100.0409

H 1= 785.4070

W 1= 50.56291

A 1= 42272.53

PASS # 6 REL STD ERROR (%) = 1.488278

P 1= 100.0209

H 1= 792.4382

W 1= 50.26468

A 1= 42399.40

PASS # 7 REL STD ERROR (%) = .7490875

P 1= 100.0107

H 1= 796.3331

W 1= 50.11883

A 1= 42484.25

FIGURE 13a: Gaussian Peak With Position Estimate Error

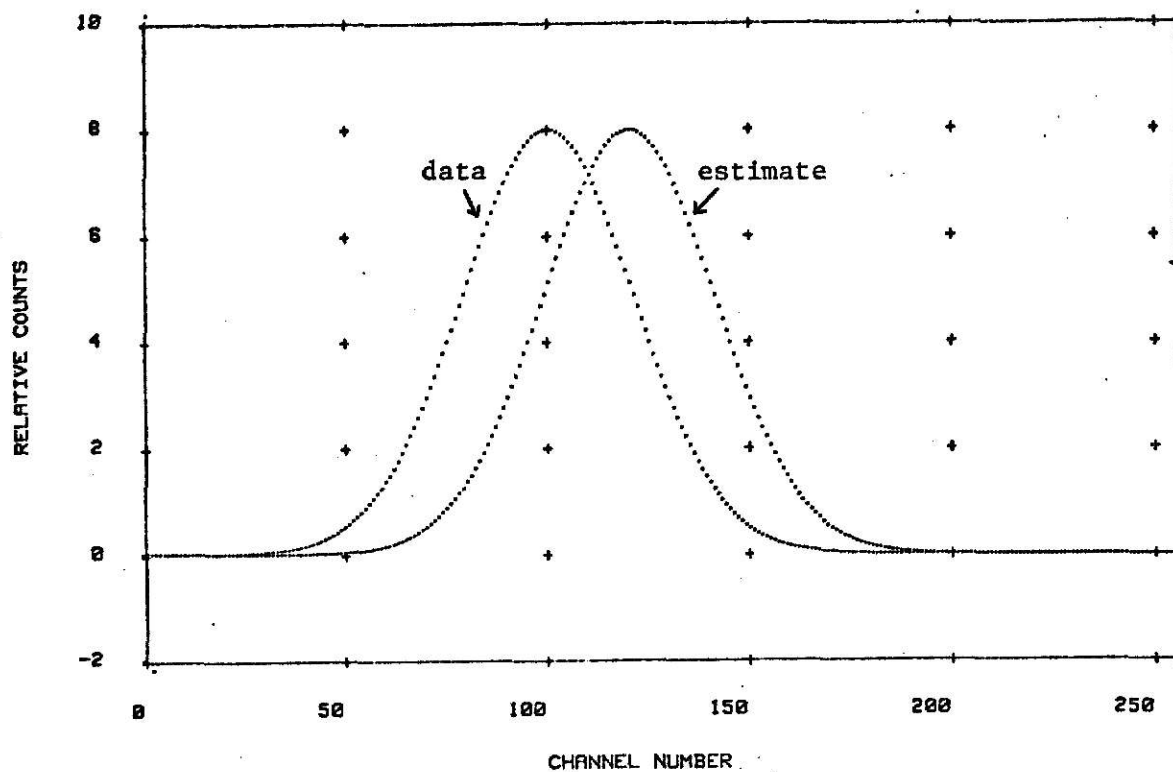


FIGURE 13b: Starting Data and Estimate

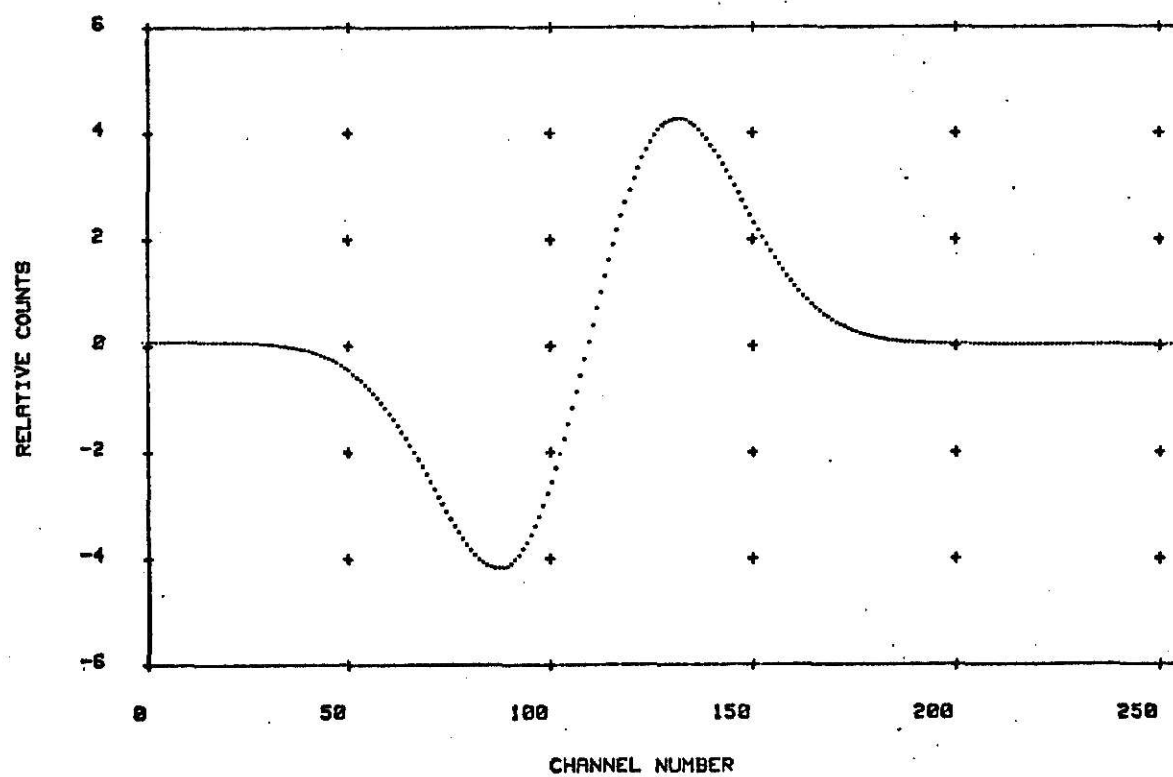


FIGURE 13c: Starting Error

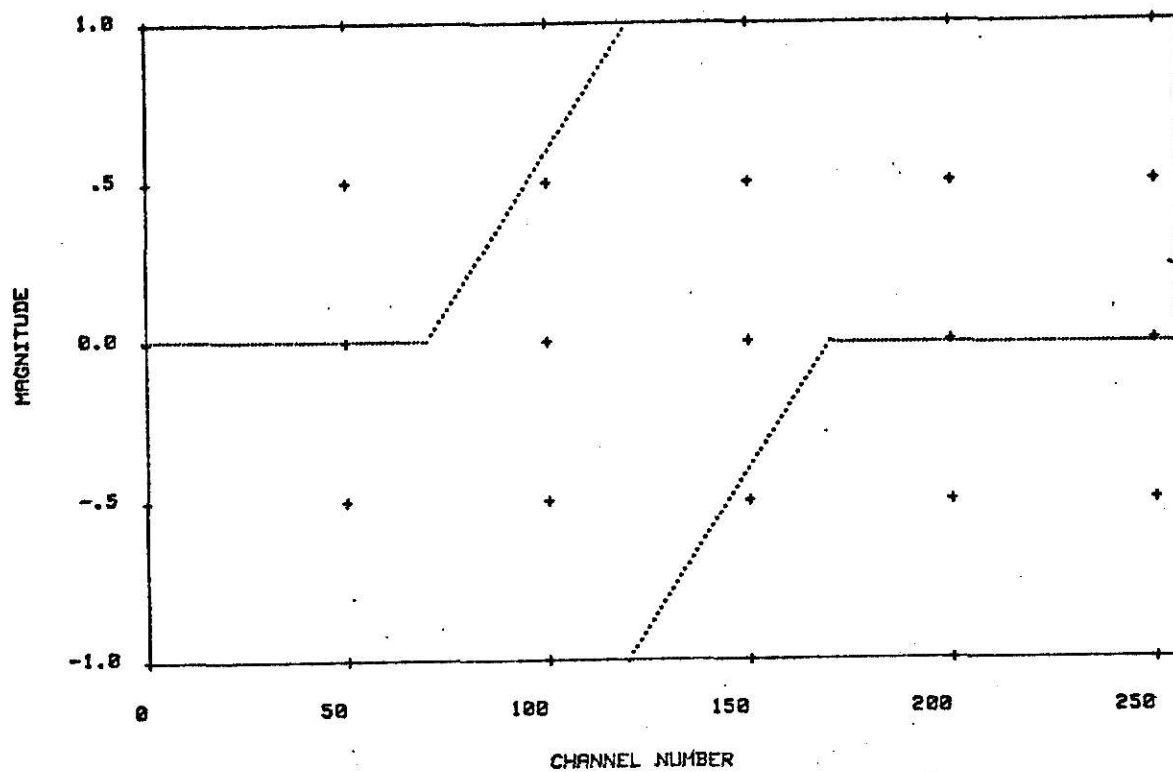


FIGURE 13d: Position Filter

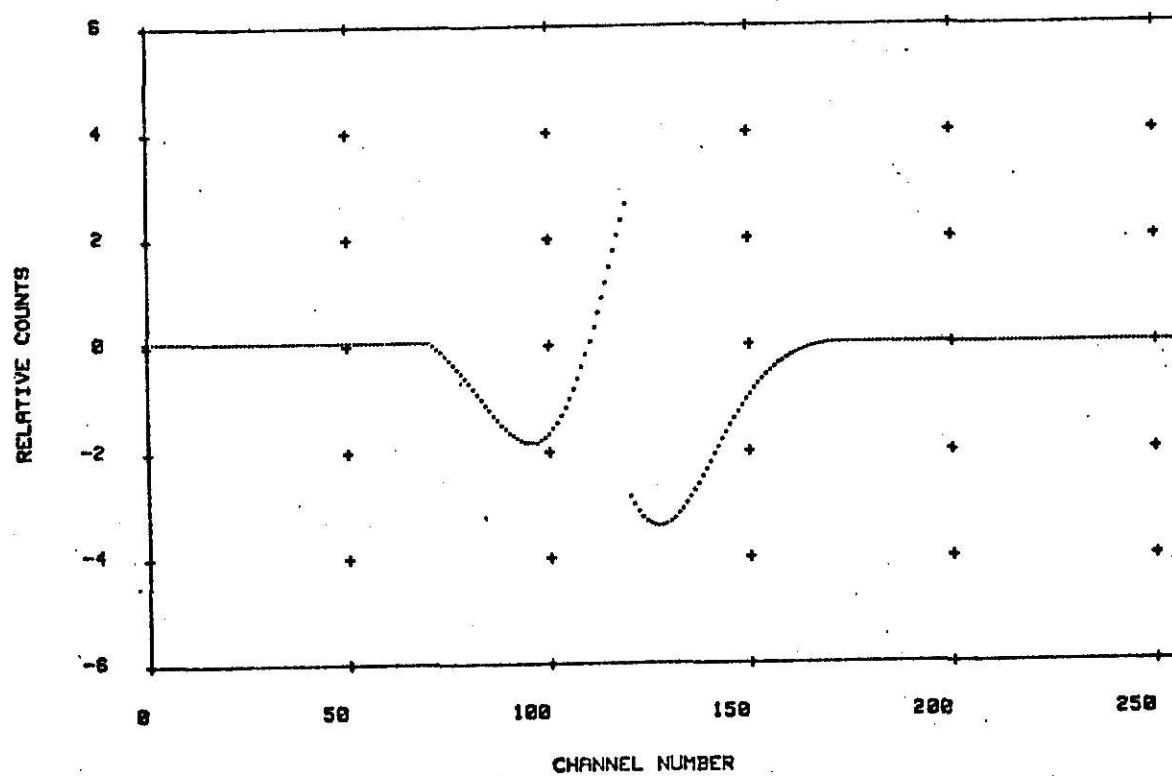


FIGURE 13e: Position Filter x Error

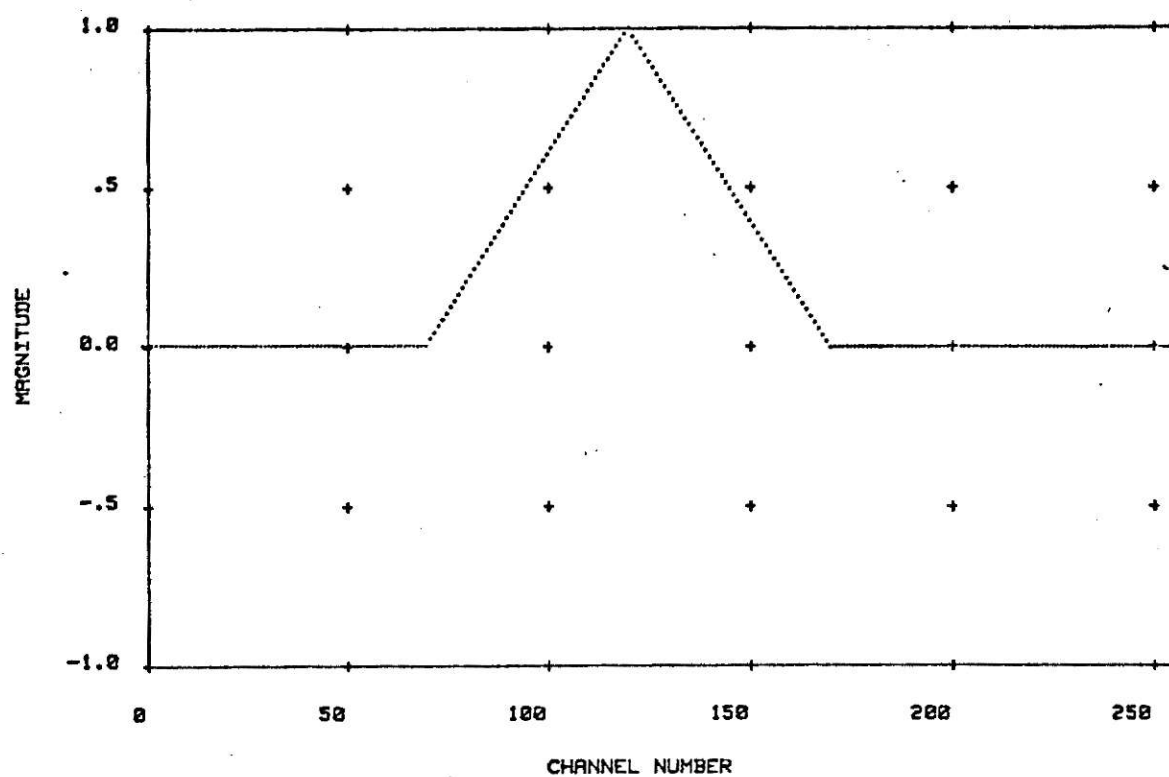


FIGURE 13f: Height Filter

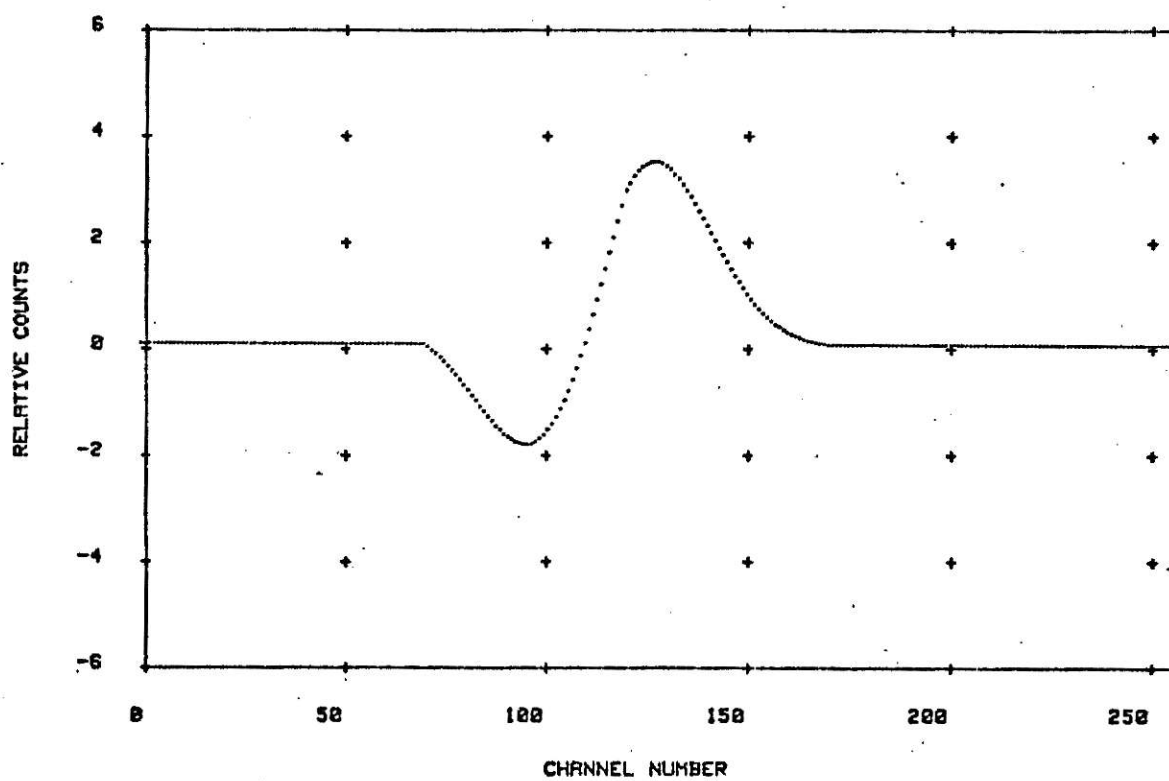


FIGURE 13g: Height Filter x Error

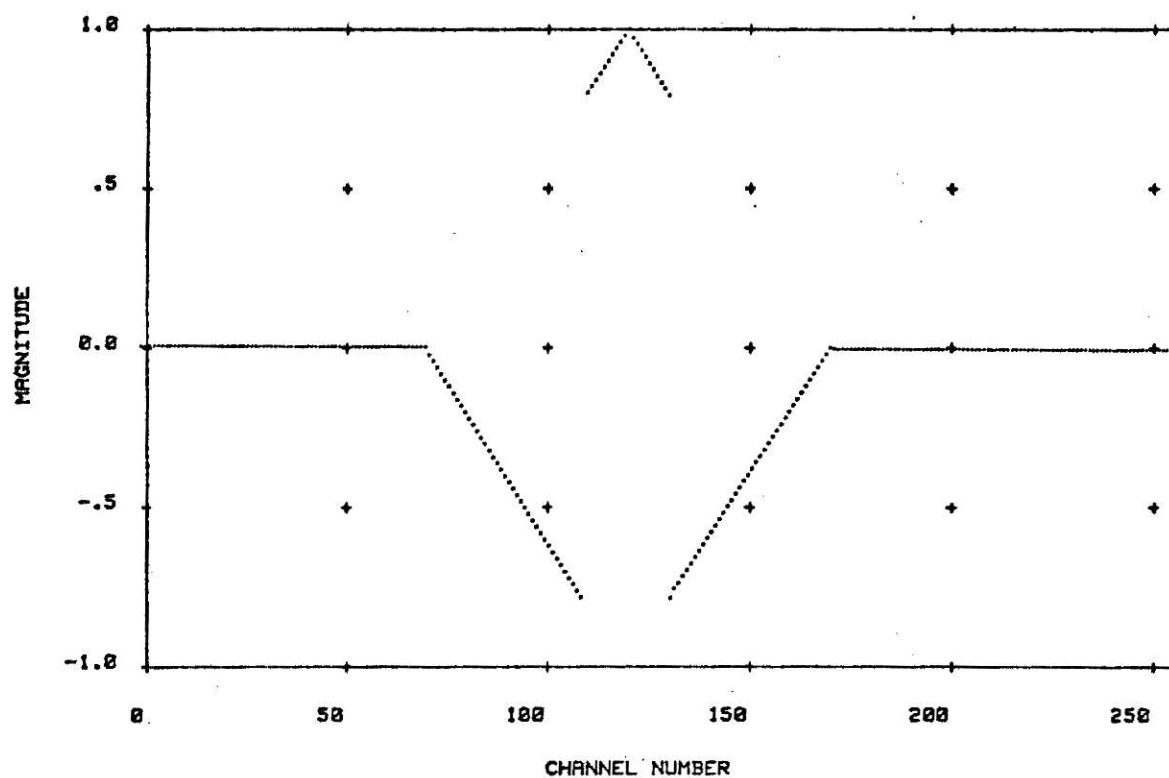


FIGURE 13h: Width Filter

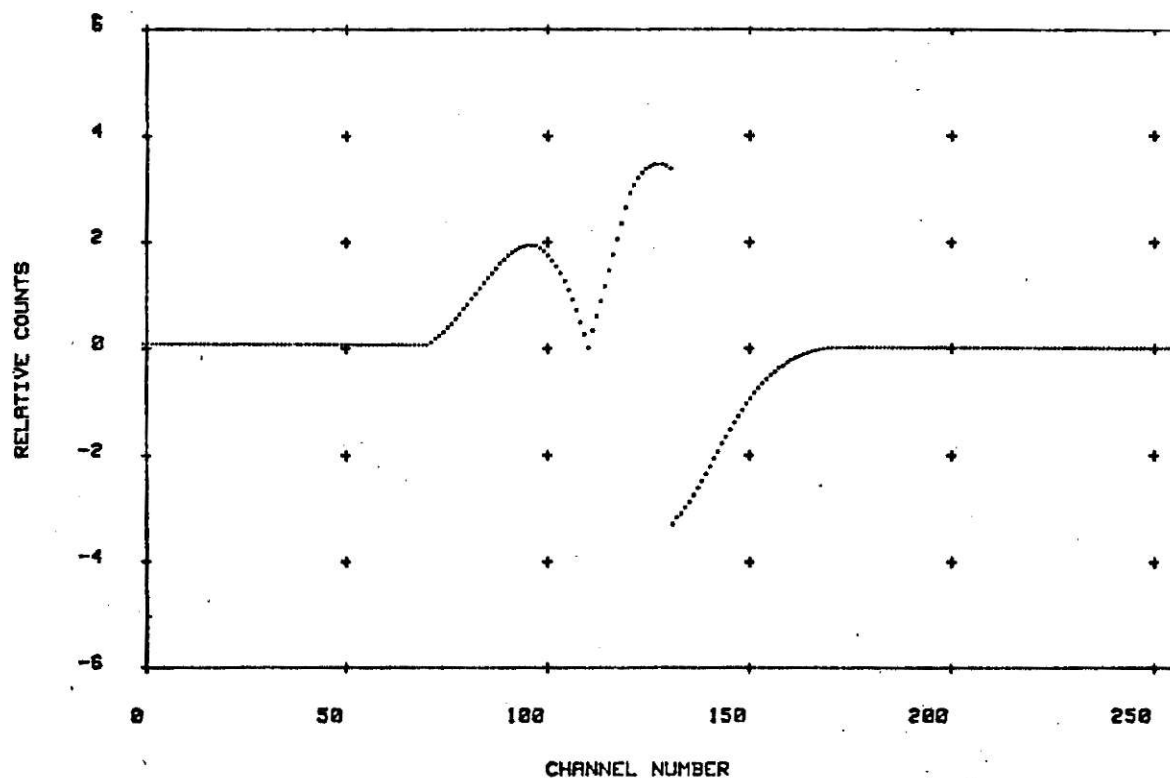


FIGURE 13i: Width Filter x Error

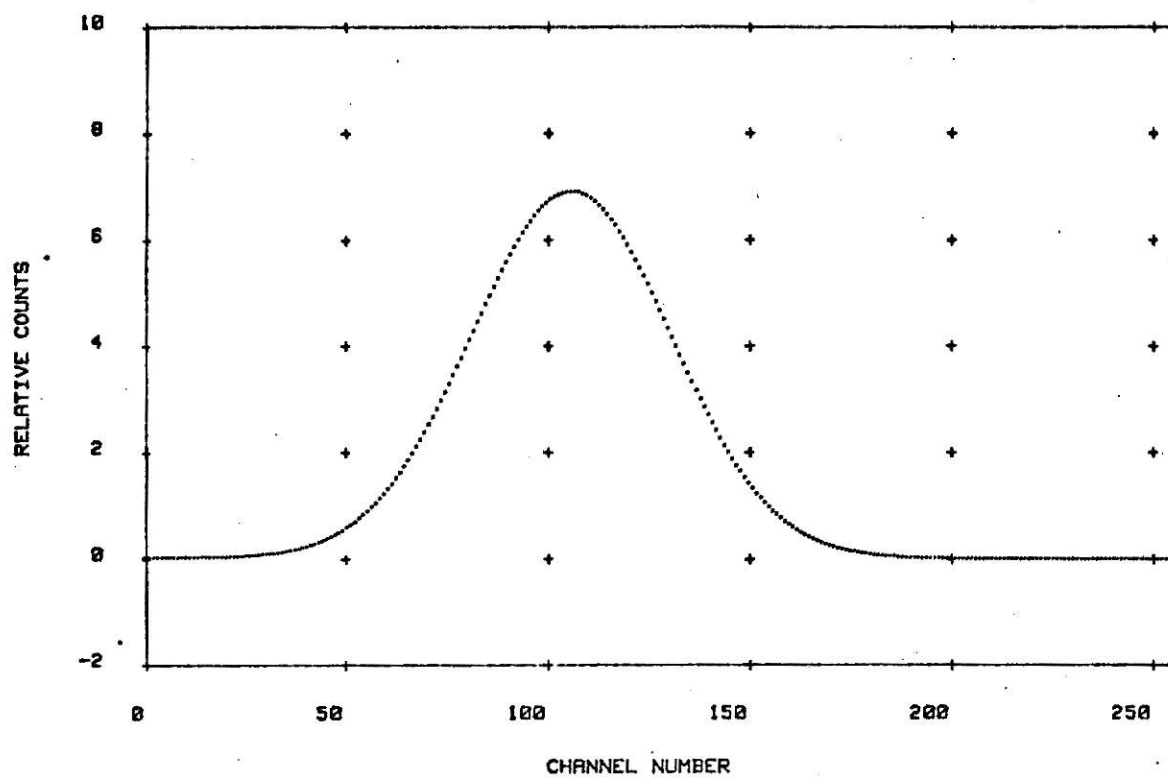


FIGURE 13j: Estimate After First Iteration

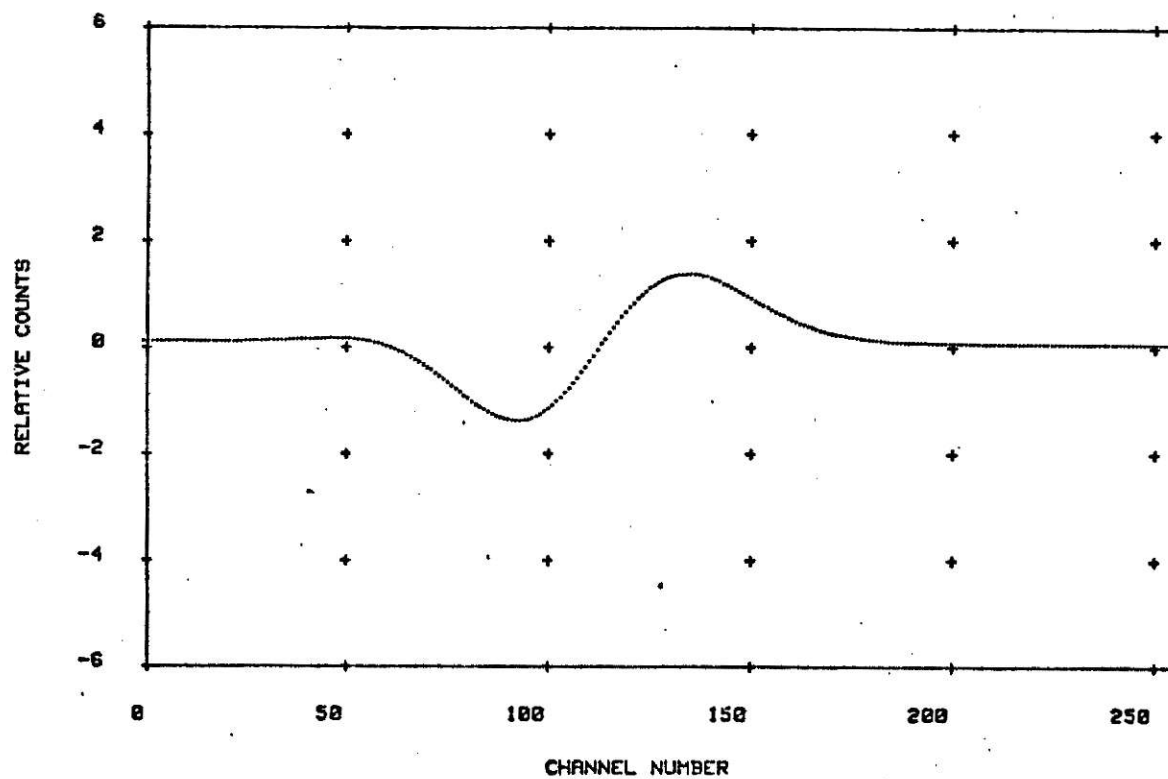


FIGURE 13k: Error After First Iteration

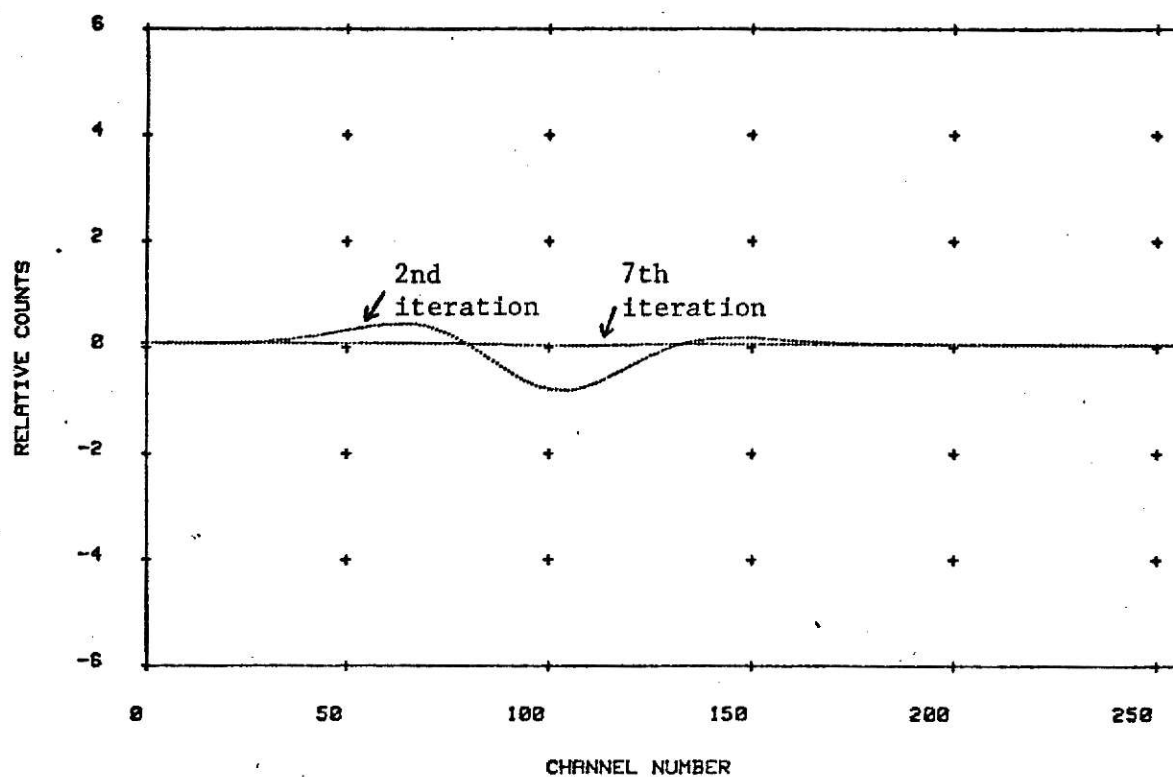


FIGURE 13l: Error After 2nd and 7th Iterations

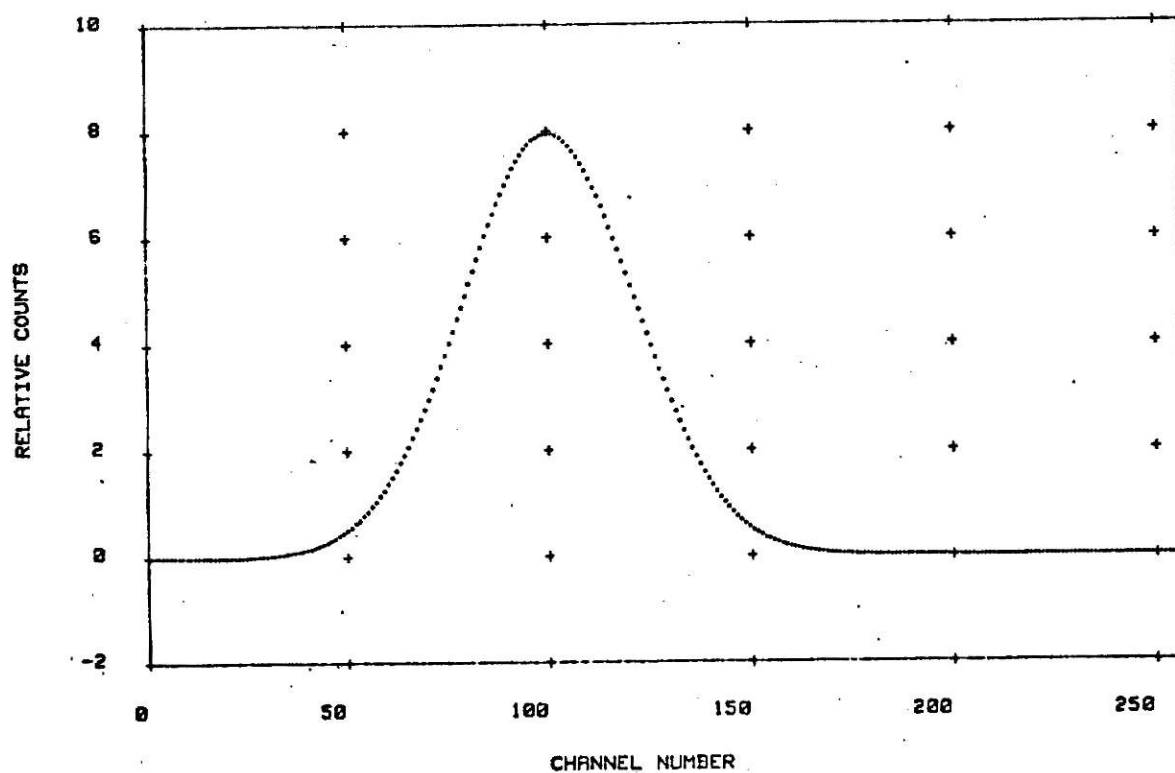


FIGURE 13m: Estimate After 7 Iterations

SP01. ARTIFICIAL GAUSSIAN SPECTRUM

P1= 100.0000 H1= 800.0000 W1= 50.00000

P-P NOISE= 0.000000

PLOTTER SCALE FACTOR (COUNTS/DIV): 100

IMGL. NORMALIZED GAUSSIAN IMAGE

AREA = 42578.63

PASS # 0 REL STD ERROR (%) = 36.84841

P 1= 100.0000 H 1= 960.0001 W 1= 50.00000 A 1= 51094.45

PASS # 1 REL STD ERROR (%) = 11.28785

P 1= 99.83333 H 1= 847.0376 W 1= 50.21090 A 1= 45272.26

PASS # 2 REL STD ERROR (%) = 3.126071

P 1= 99.83834 H 1= 812.5318 W 1= 50.05623 A 1= 43292.60

PASS # 3 REL STD ERROR (%) = .8438055

P 1= 99.95009 H 1= 803.4121 W 1= 50.01390 A 1= 42772.14

PASS # 4 REL STD ERROR (%) = .2218463

P 1= 99.98581 H 1= 801.0071 W 1= 49.99824 A 1= 42630.79

PASS # 5 REL STD ERROR (%) = 5.965611E-02

P 1= 99.99629 H 1= 800.3939 W 1= 49.99117 A 1= 42592.14

PASS # 6 REL STD ERROR (%) = 2.914736E-02

P 1= 99.99910 H 1= 800.2552 W 1= 49.98767 A 1= 42581.79

PASS # 7 REL STD ERROR (%) = 2.673743E-02

P 1= 99.99975 H 1= 800.2350 W 1= 49.98609 A 1= 42579.36

FIGURE 14a: Gaussian Peak With Height Estimate Error

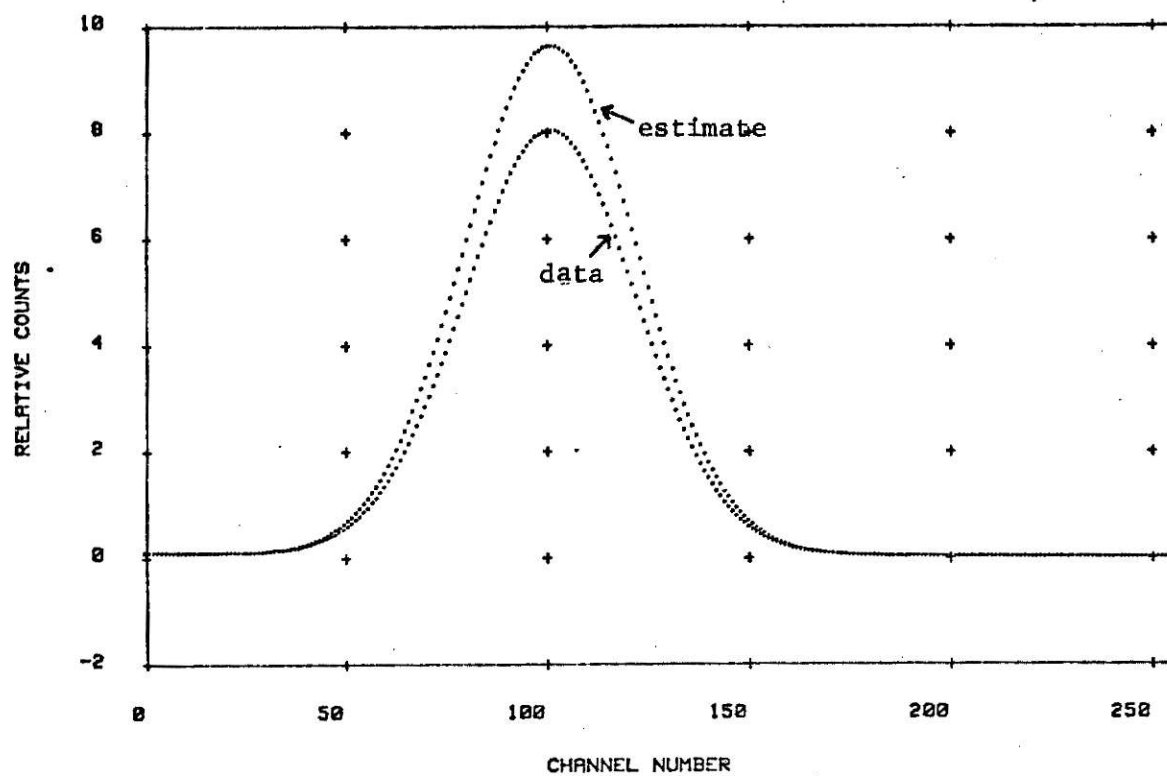


FIGURE 14b: Starting Data and Estimate

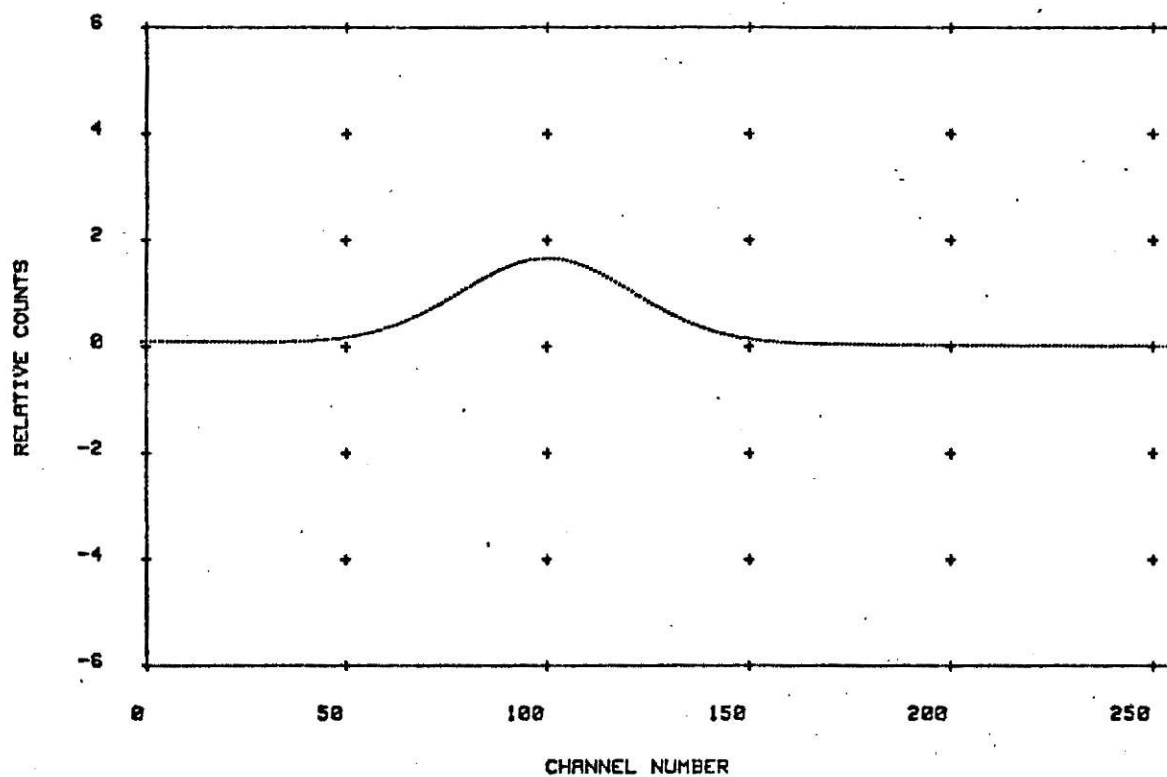


FIGURE 14c: Starting Error

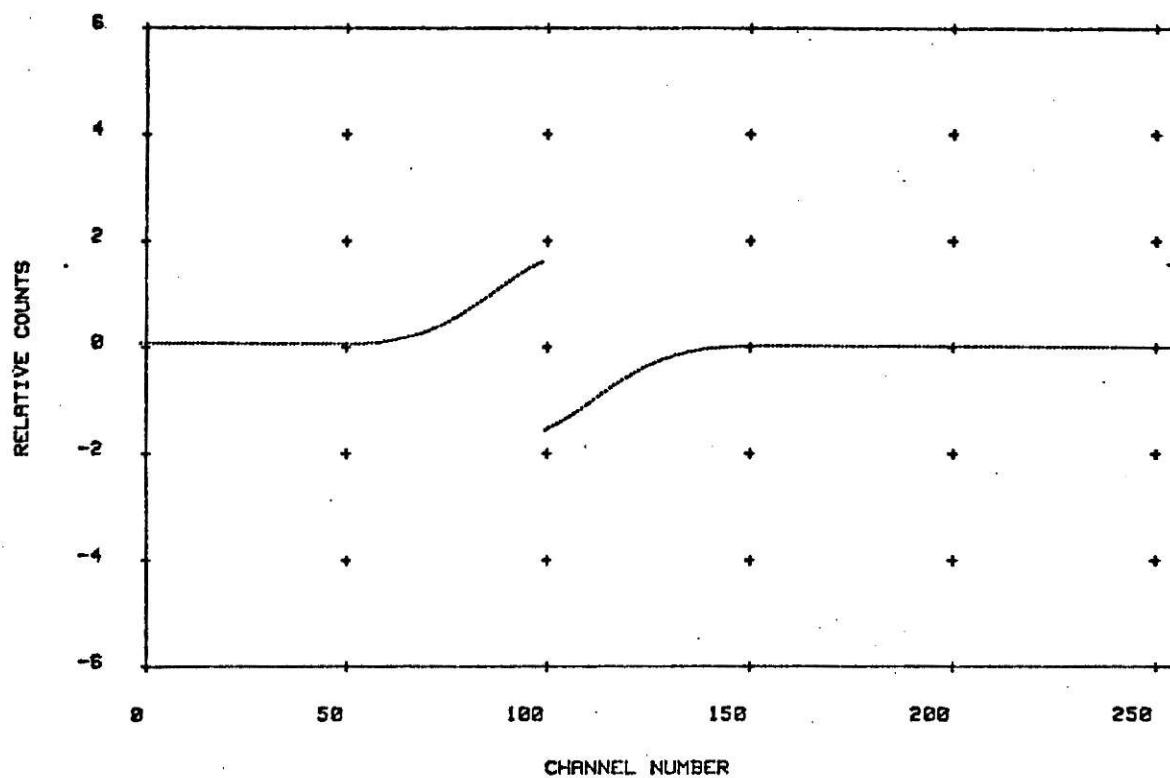


FIGURE 14d: Position Filter x Error

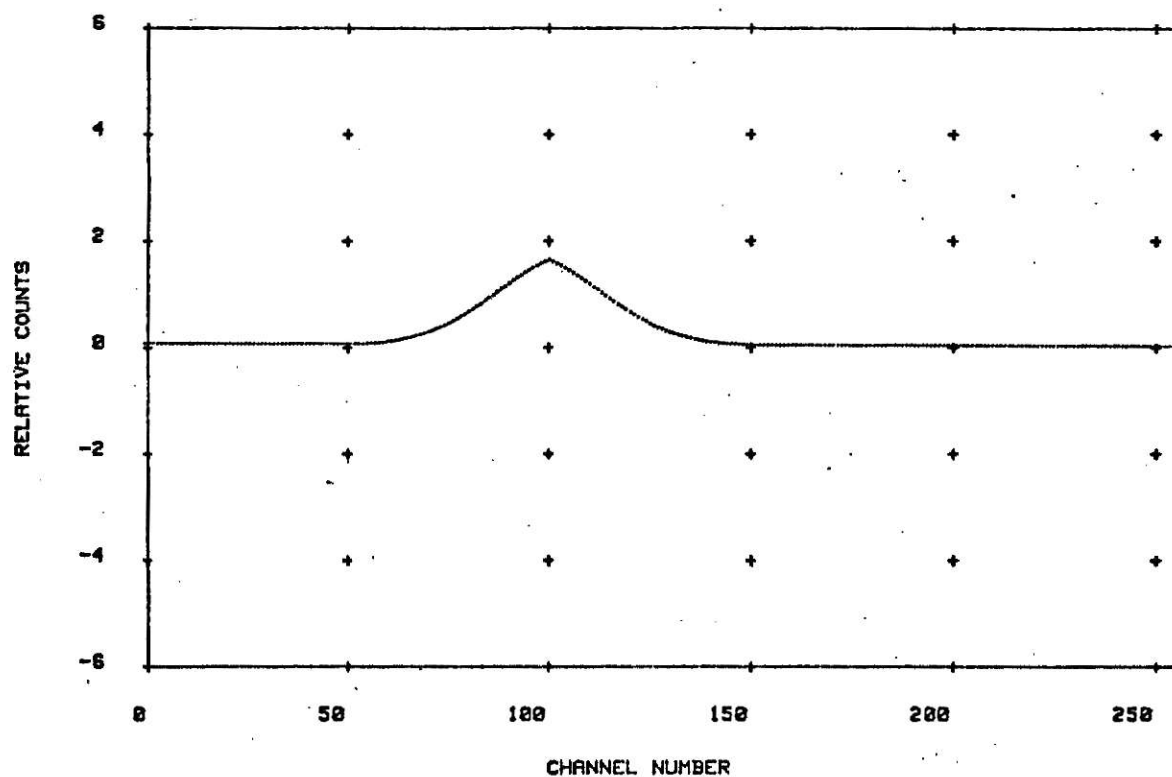


FIGURE 14e: Height Filter x Error

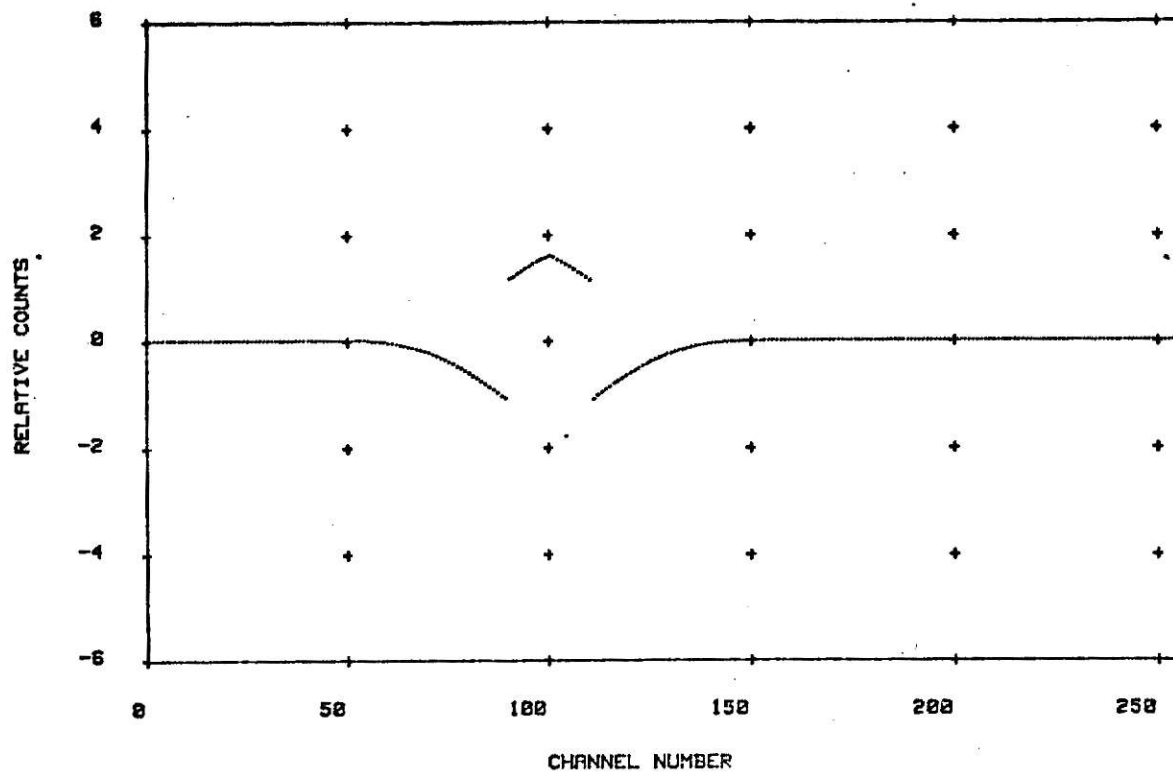


FIGURE 14f: Width Filter x Error

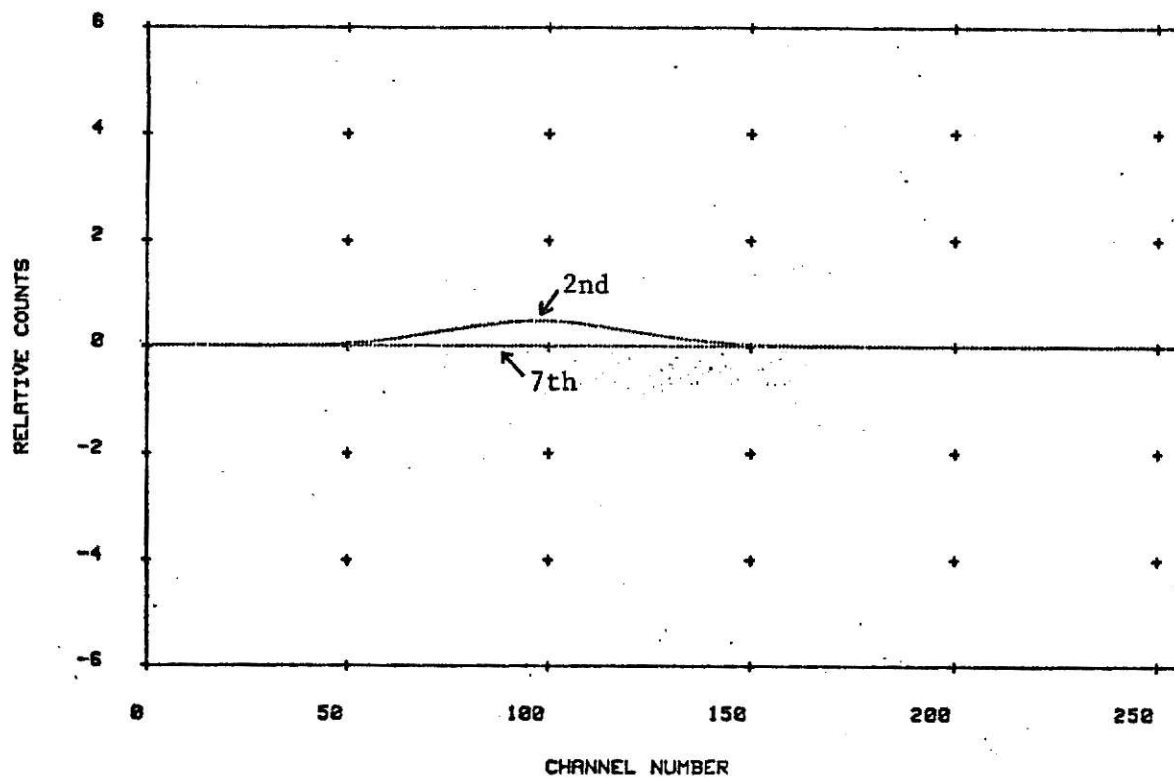


FIGURE 14g: Error After 2nd and 7th Iterations

SP01. ARTIFICIAL GAUSSIAN SPECTRUM

P1= 100.0000

H1= 800.0000

W1= 50.00000

P-P NOISE= 0.000000

PLOTTER SCALE FACTOR (COUNTS/DIV): 100

IMG1. NORMALIZED GAUSSIAN IMAGE

AREA = 42578.63

PASS # 0 REL STD ERROR (%) = 30.39851

P 1= 100.0000

H 1= 800.0000

W 1= 60.00000

A 1= 51092.35

PASS # 1 REL STD ERROR (%) = 12.68345

P 1= 100.0000

H 1= 744.4253

W 1= 54.75191

A 1= 43385.95

PASS # 2 REL STD ERROR (%) = 8.446452

P 1= 100.0746

H 1= 756.4255

W 1= 52.31130

A 1= 42120.36

PASS # 3 REL STD ERROR (%) = 4.995665

P 1= 100.0622

H 1= 773.9428

W 1= 51.13170

A 1= 42124.02

PASS # 4 REL STD ERROR (%) = 2.735832

P 1= 100.0374

H 1= 785.8401

W 1= 50.54549

A 1= 42281.26

PASS # 5 REL STD ERROR (%) = 1.444703

P 1= 100.0202

H 1= 792.6669

W 1= 50.25620

A 1= 42404.49

PASS # 6 REL STD ERROR (%) = .7270522

P 1= 100.0104

H 1= 796.4488

W 1= 50.11479

A 1= 42406.94

PASS # 7 REL STD ERROR (%) = .3609070

P 1= 100.0050

H 1= 798.3755

W 1= 50.04643

A 1= 42531.65

FIGURE 15a: Gaussian Peak With Width Estimate Error

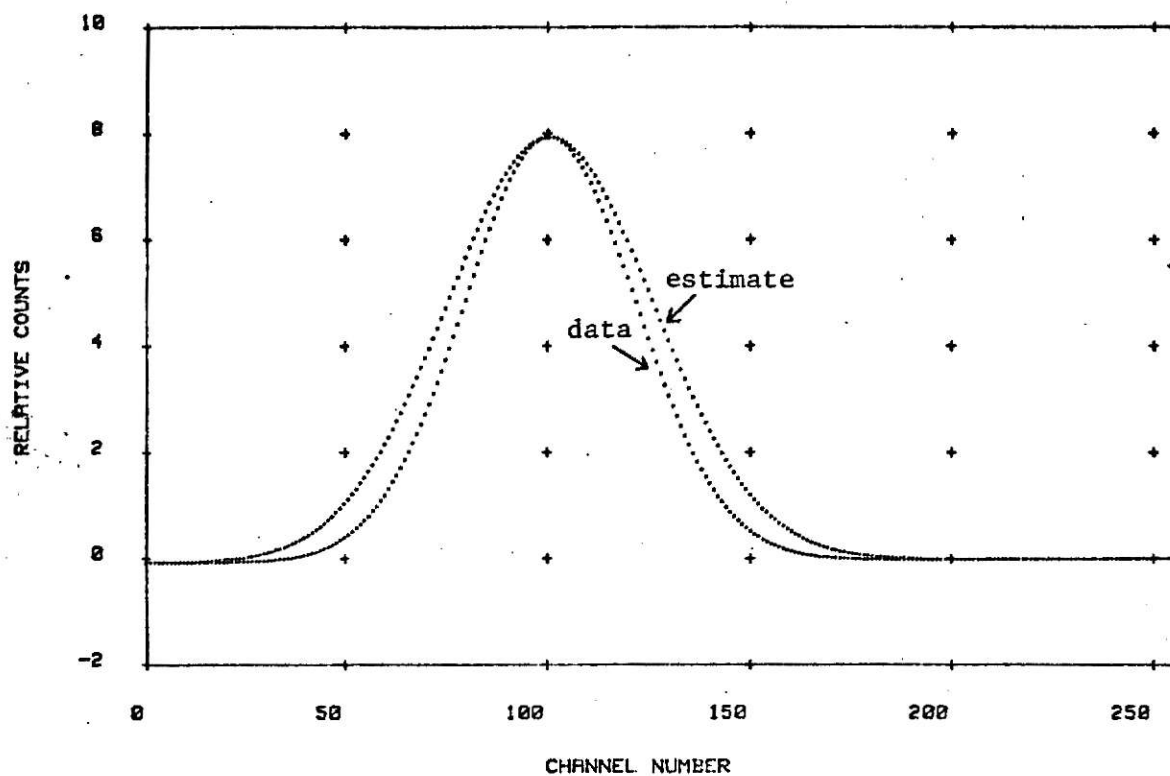


FIGURE 15b: Starting Data and Estimate

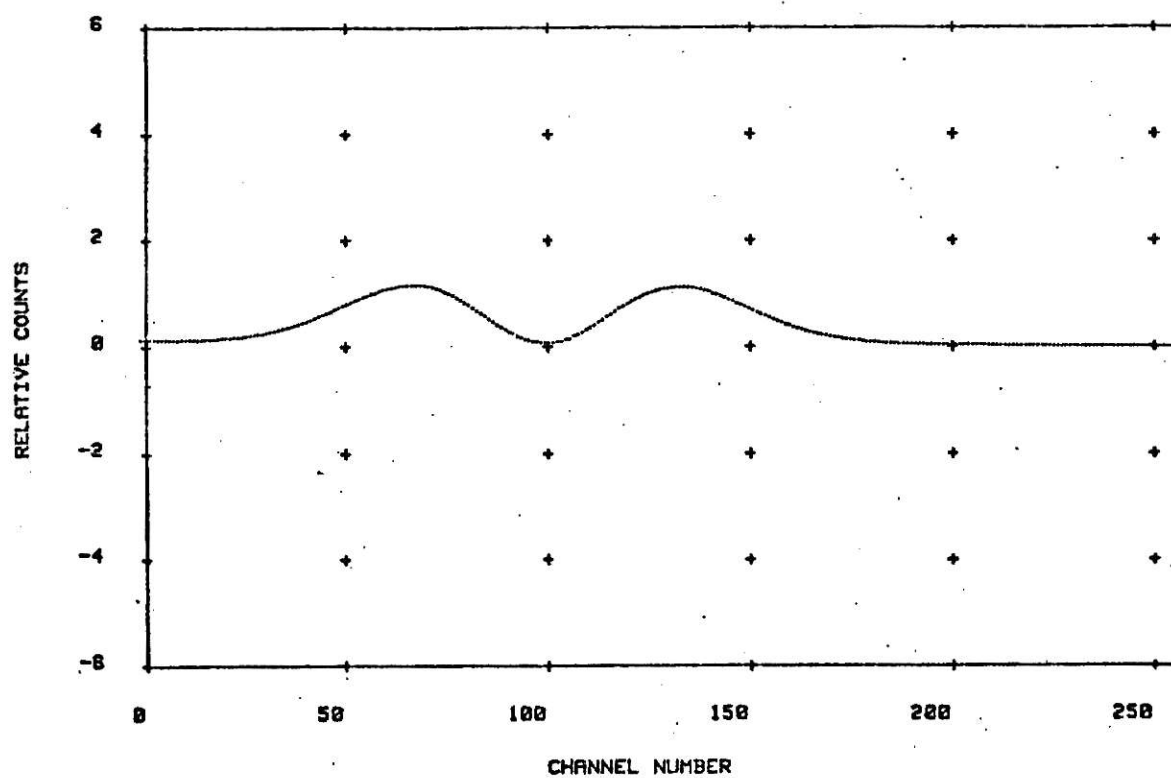


FIGURE 15c: Starting Error

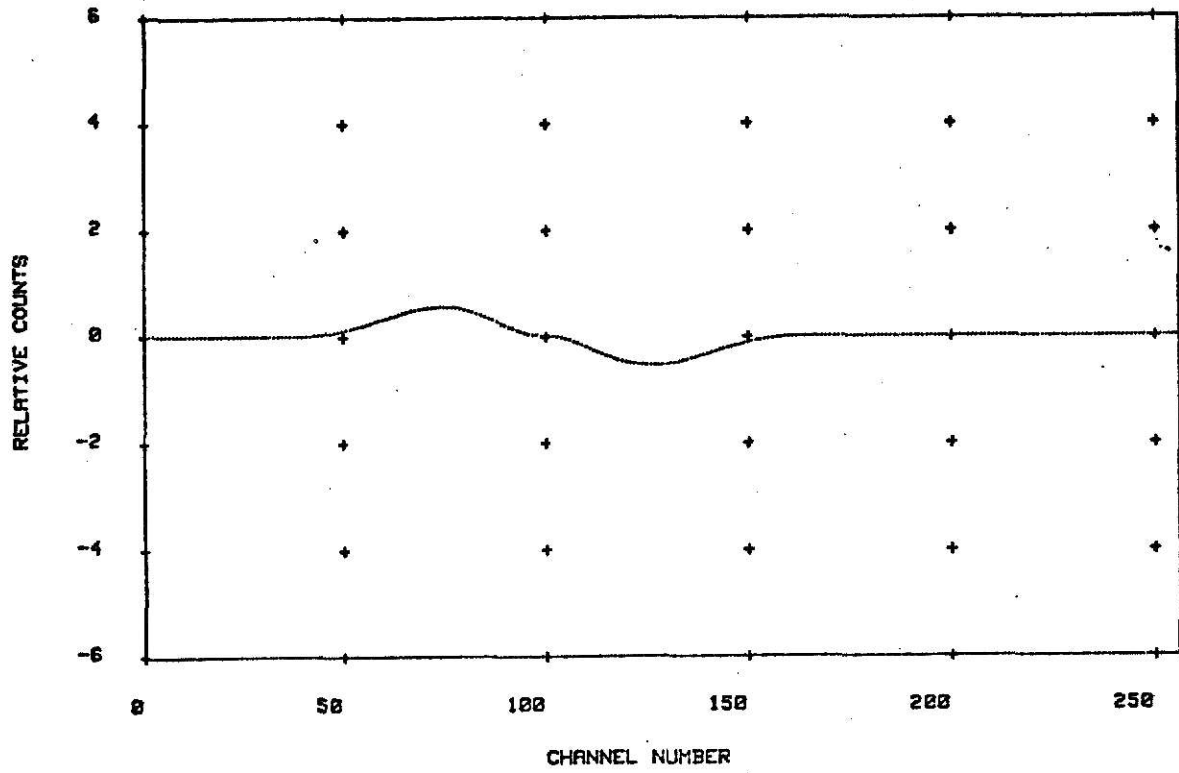


FIGURE 15d: Position Filter x Error

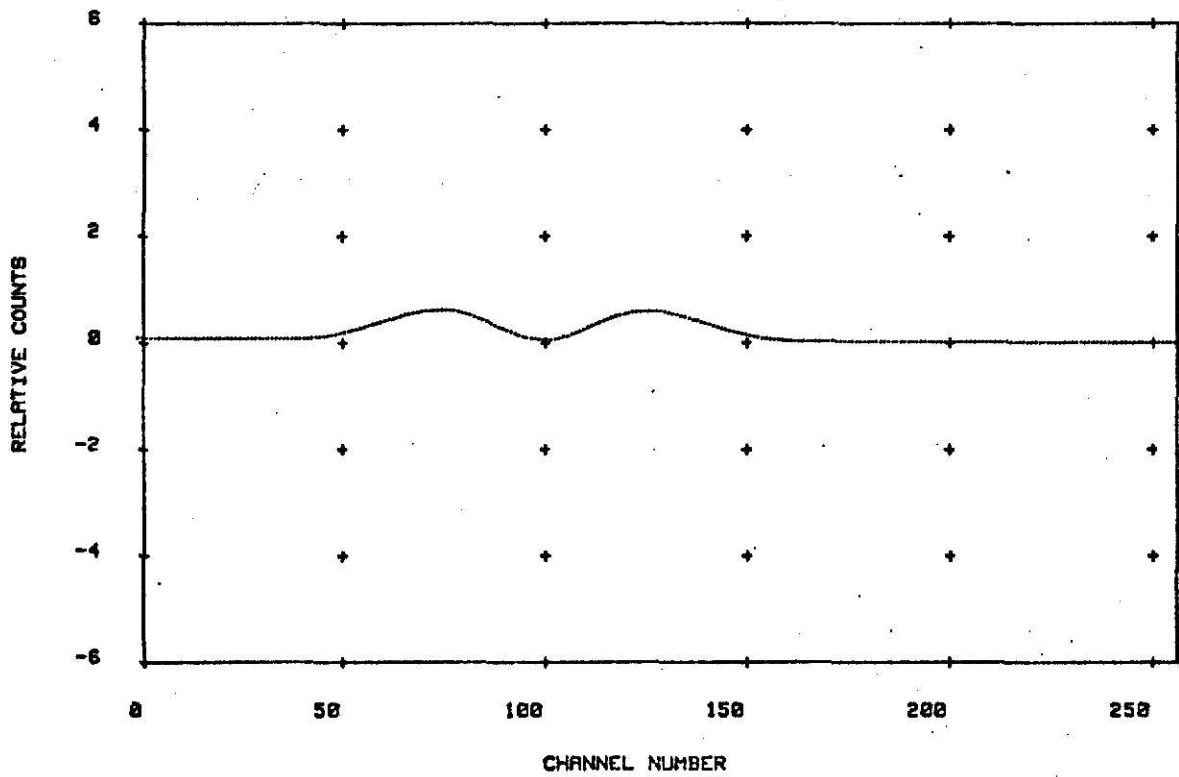


FIGURE 15e: Height Filter x Error

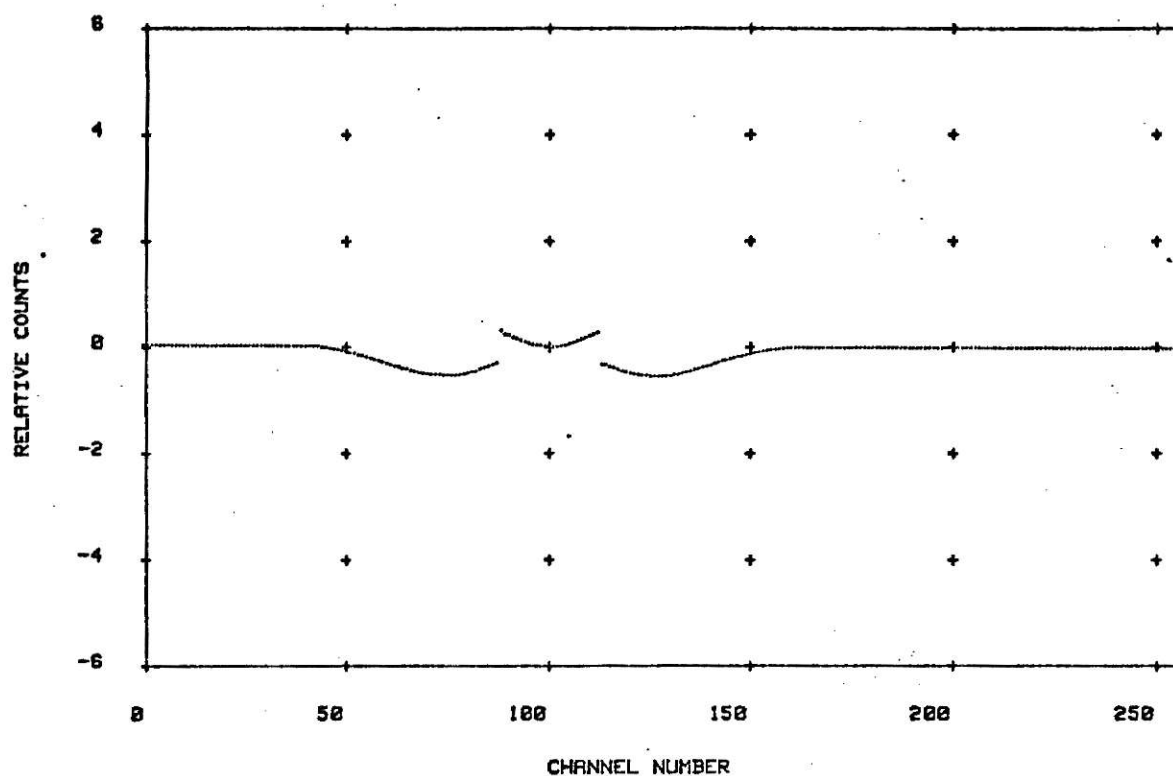


FIGURE 15f: Width Filter x Error

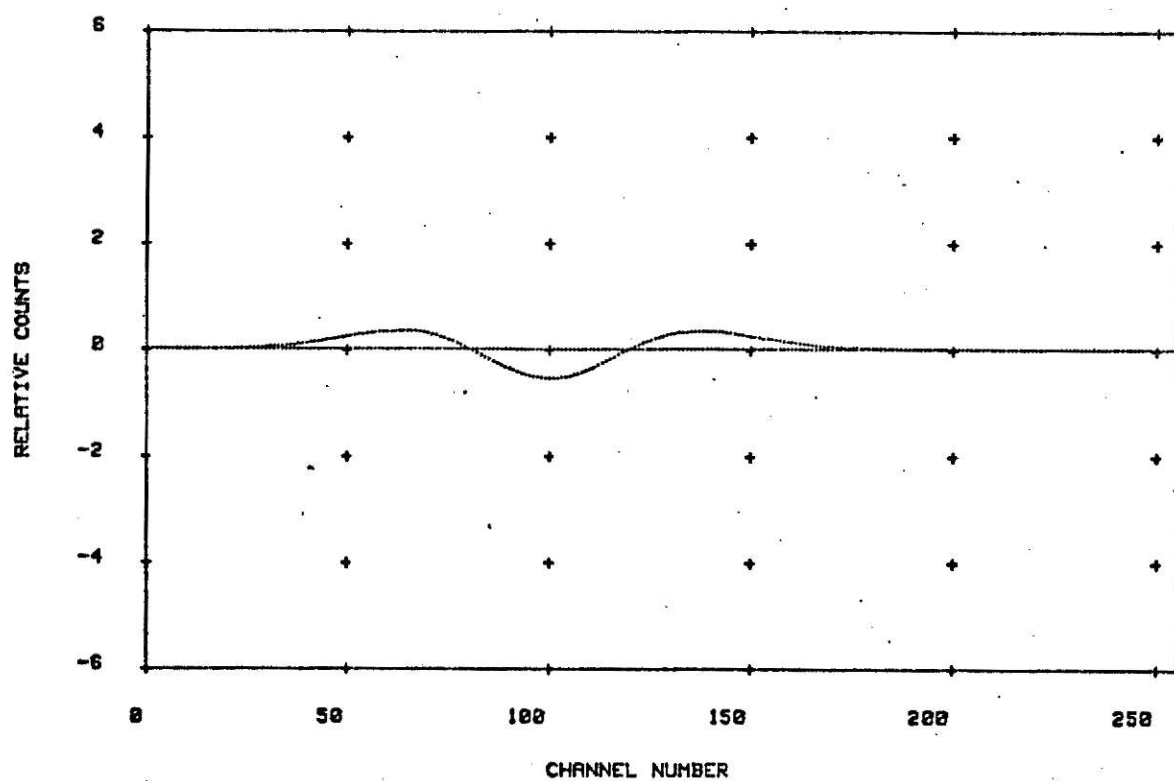


FIGURE 15g: Error After 2nd and 7th Iterations

SP02, ARTIFICIAL GAUSSIAN SPECTRUM - 2 PEAKS

P1= 100.0000 H1= 200.0000 W1= 25.00000
 P2= 150.0000 H2= 800.0000 W2= 50.00000
 P-P NOISE= 0.000000

PLOTTER SCALE FACTOR (COUNTS/DIV): 100

IMG1, NORMALIZED GAUSSIAN IMAGE

AREA = 47901.02

PASS # 0 REL STD ERROR (%) = 103.0239

P 1= 90.00000	H 1= 240.0000	W 1= 30.00000	A 1= 7664.177
P 2= 165.0000	H 2= 960.0001	W 2= 60.00000	A 2= 61301.54

PASS # 1 REL STD ERROR (%) = 31.36615

P 1= 97.82307	H 1= 186.7345	W 1= 34.60061	A 1= 6877.693
P 2= 152.4752	H 2= 746.2026	W 2= 62.23076	A 2= 49427.71

PASS # 2 REL STD ERROR (%) = 15.90954

P 1= 97.03520	H 1= 130.7141	W 1= 27.31252	A 1= 3000.288
P 2= 149.8765	H 2= 712.1383	W 2= 55.03218	A 2= 41716.89

PASS # 3 REL STD ERROR (%) = 9.367503

P 1= 100.3898	H 1= 152.4992	W 1= 25.17003	A 1= 4085.874
P 2= 149.9288	H 2= 750.9954	W 2= 52.89908	A 2= 42287.98

PASS # 4 REL STD ERROR (%) = 5.589344

P 1= 99.57193	H 1= 172.9606	W 1= 24.57087	A 1= 4523.738
P 2= 150.0351	H 2= 771.0299	W 2= 51.65420	A 2= 42394.40

PASS # 5 REL STD ERROR (%) = 2.953996

P 1= 99.93530	H 1= 186.4640	W 1= 24.51541	A 1= 4865.960
P 2= 149.9026	H 2= 783.8776	W 2= 51.01550	A 2= 42567.91

PASS # 6 REL STD ERROR (%) = 1.799341

P 1= 99.85135	H 1= 192.2055	W 1= 24.60241	A 1= 5033.404
P 2= 149.9879	H 2= 790.4593	W 2= 50.59976	A 2= 42575.50

PASS # 7 REL STD ERROR (%) = 1.028848

P 1= 99.92404	H 1= 196.0901	W 1= 24.67340	A 1= 5150.117
P 2= 149.9851	H 2= 794.5248	W 2= 50.36658	A 2= 42597.28

FIGURE 16a: Overlapped Gaussian Peaks

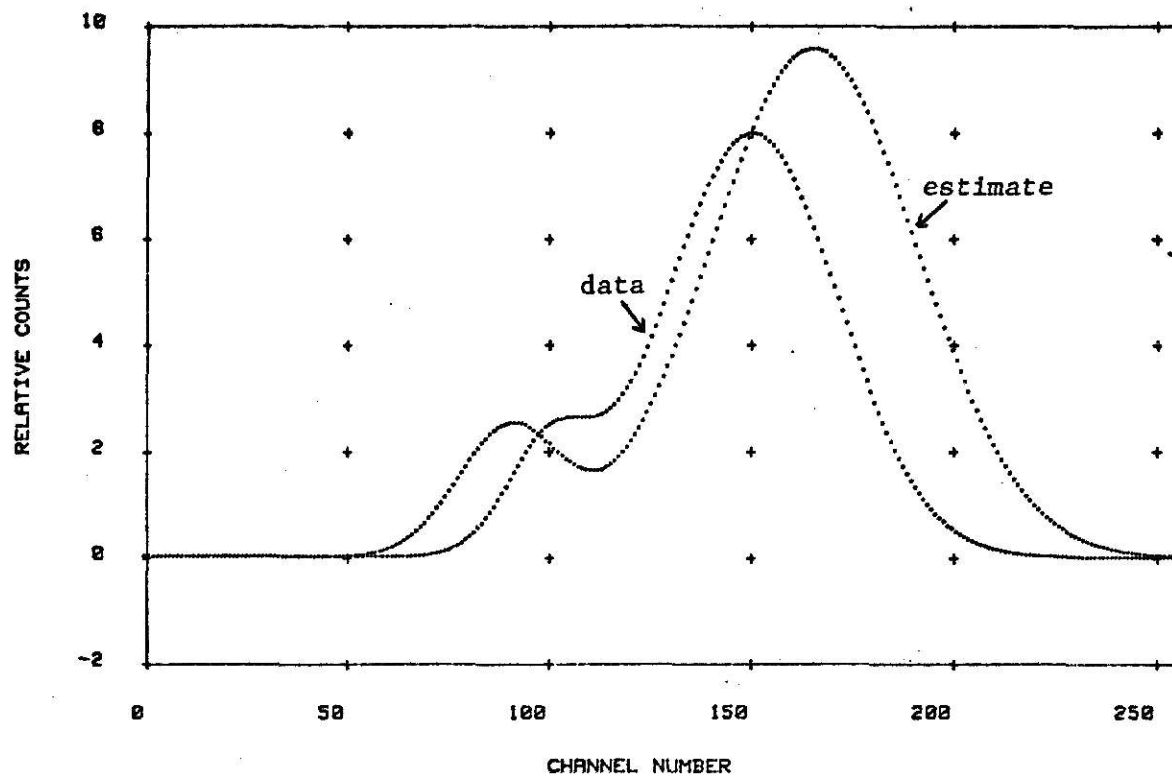


FIGURE 16b: Data and Starting Estimate

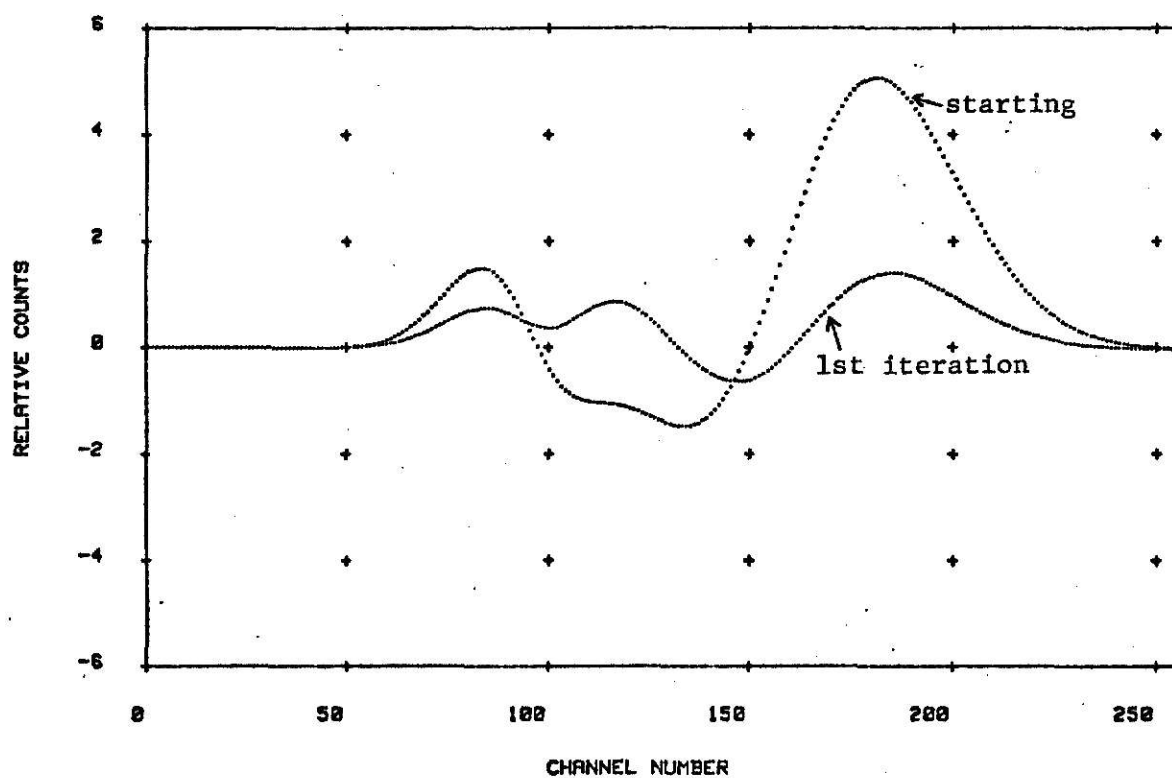


FIGURE 16c: Starting Error and Error After First Iteration

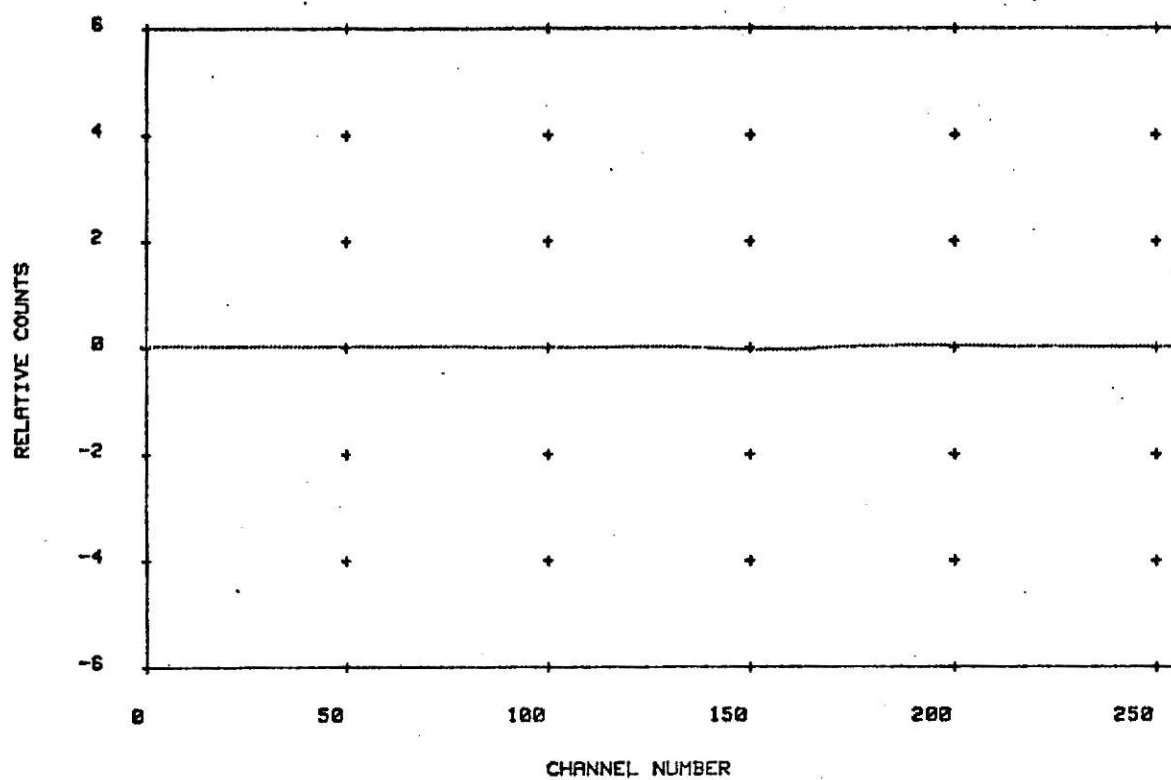


FIGURE 16d: Error After 7th Iteration

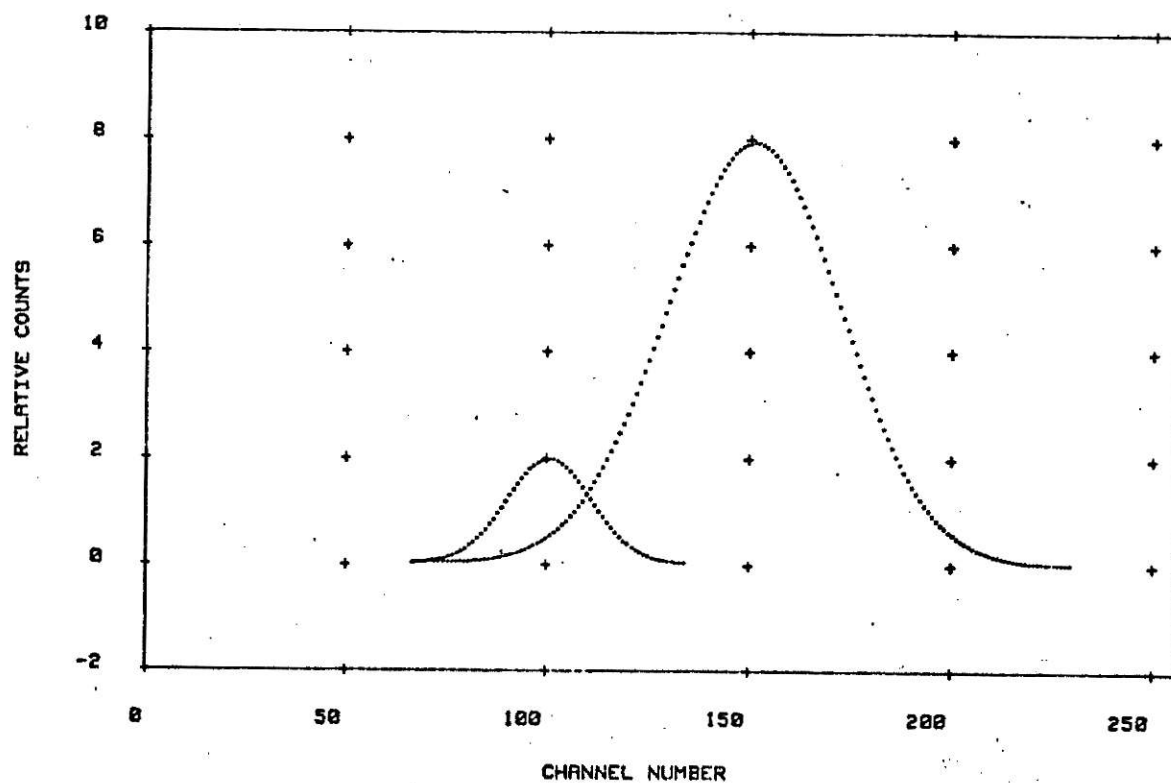


FIGURE 16e: Individual Peak Estimates After 7 Iterations

SP03, ARTIFICIAL GAUSSIAN SPECTRUM -- 2 PEAKS + NOISE

P1= 100.0000 H1= 200.0000 W1= 25.00000
 P2= 150.0000 H2= 800.0000 W2= 50.00000
 P-P NOISE= 100.0000

PLOTTER SCALE FACTOR (COUNTS/DIV): 100

IMG1, NORMALIZED GAUSSIAN IMAGE

AREA = 47038.46

PASS # 0 REL STD ERROR (%) = 107.8152

P 1= 90.00000	H 1= 240.0000	W 1= 30.00000	A 1= 7664.177
P 2= 165.0000	H 2= 960.0001	W 2= 60.00000	A 2= 61301.54

PASS # 1 REL STD ERROR (%) = 34.83976

P 1= 96.87293	H 1= 181.9416	W 1= 33.97510	A 1= 6579.983
P 2= 152.4208	H 2= 740.3926	W 2= 62.30794	A 2= 49103.90

PASS # 2 REL STD ERROR (%) = 20.63973

P 1= 96.79955	H 1= 127.3591	W 1= 29.89339	A 1= 4052.672
P 2= 149.3716	H 2= 707.5895	W 2= 55.72546	A 2= 41972.38

PASS # 3 REL STD ERROR (%) = 17.06620

P 1= 99.62546	H 1= 133.7017	W 1= 28.97213	A 1= 4123.343
P 2= 149.3493	H 2= 740.9328	W 2= 53.71253	A 2= 42362.96

PASS # 4 REL STD ERROR (%) = 15.67981

P 1= 100.0186	H 1= 145.3297	W 1= 27.42650	A 1= 4242.841
P 2= 149.4772	H 2= 759.1967	W 2= 52.46729	A 2= 42400.87

PASS # 5 REL STD ERROR (%) = 14.92483

P 1= 99.80450	H 1= 158.5721	W 1= 27.64062	A 1= 4665.597
P 2= 149.4737	H 2= 771.2991	W 2= 52.01576	A 2= 42705.97

PASS # 6 REL STD ERROR (%) = 14.79374

P 1= 100.1573	H 1= 162.9721	W 1= 27.71727	A 1= 4808.316
P 2= 149.5014	H 2= 776.4672	W 2= 51.85002	A 2= 42855.23

PASS # 7 REL STD ERROR (%) = 14.70466

P 1= 99.77408	H 1= 164.6524	W 1= 27.72658	A 1= 4859.598
P 2= 149.5373	H 2= 778.2094	W 2= 51.68149	A 2= 42811.78

FIGURE 17a: Overlapped Gaussian Peaks With Noise

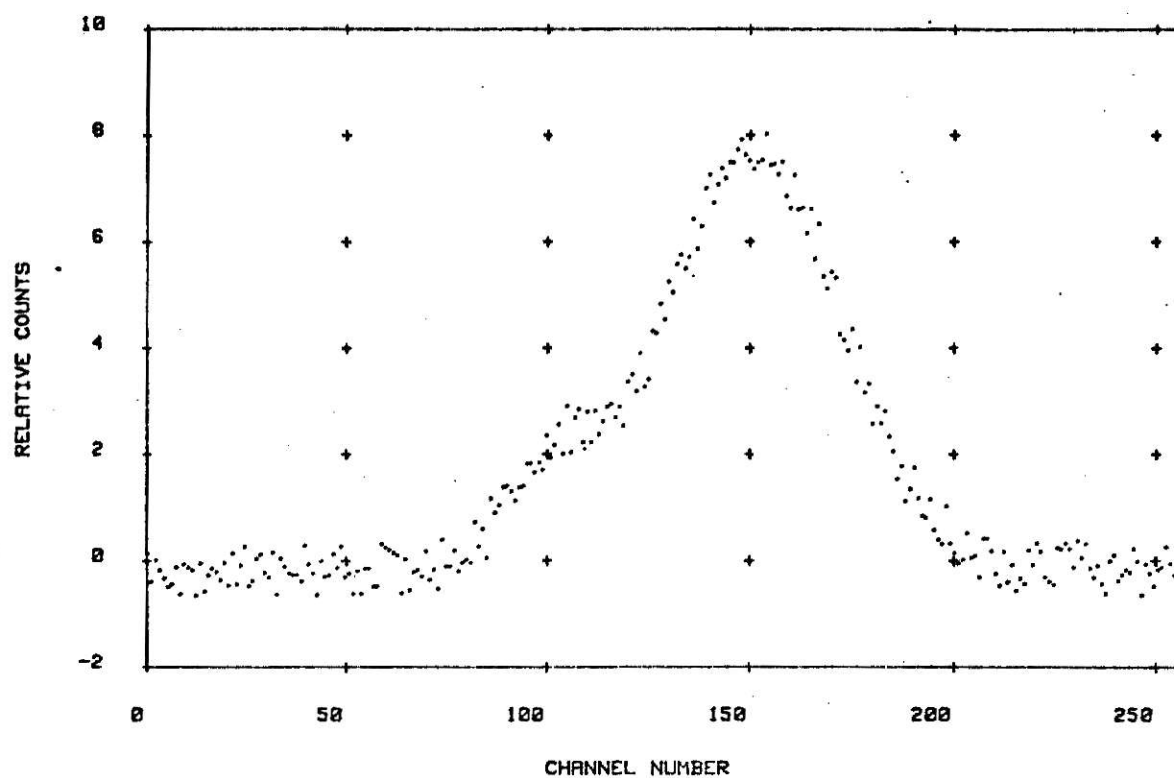


FIGURE 17b: Data

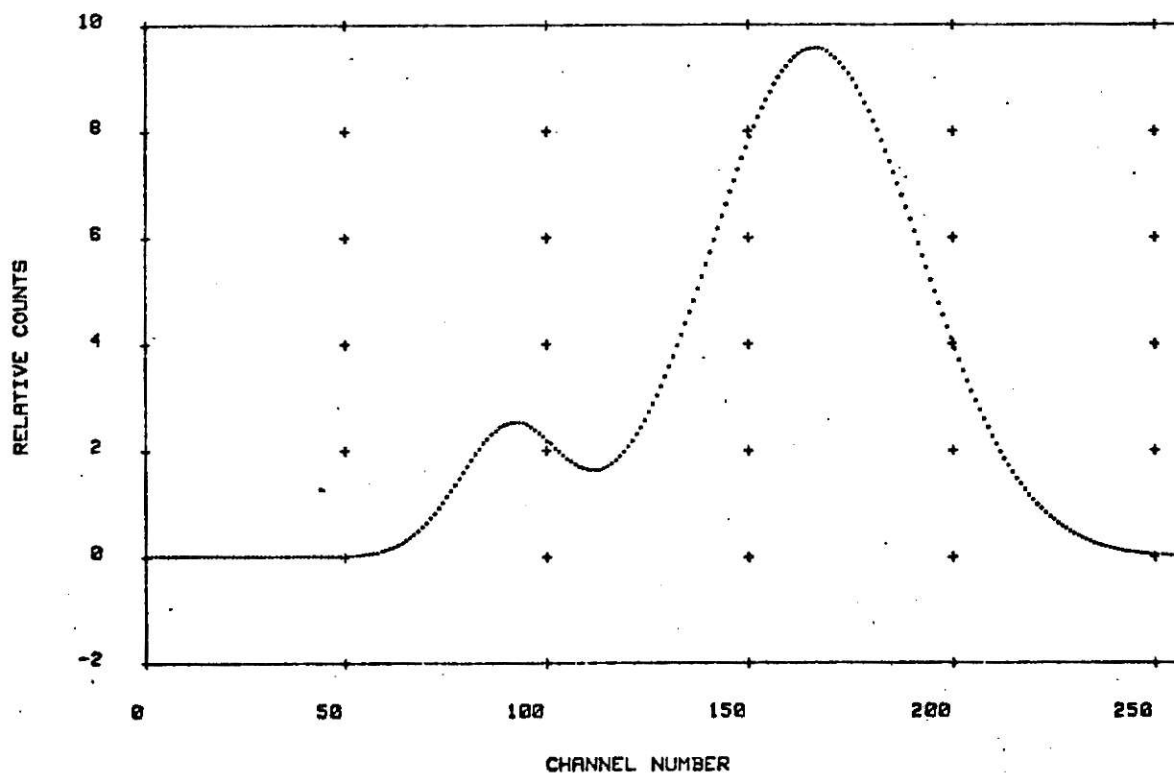


FIGURE 17c: Starting Estimate

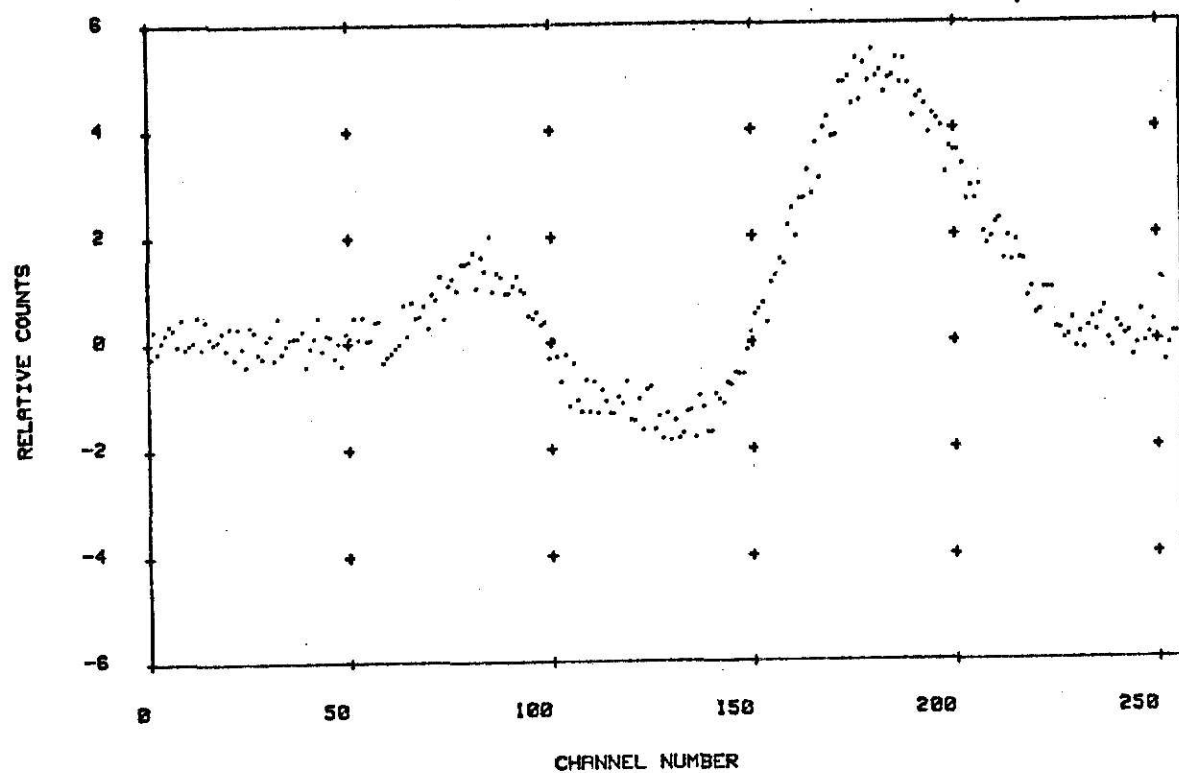


FIGURE 17d: Starting Error

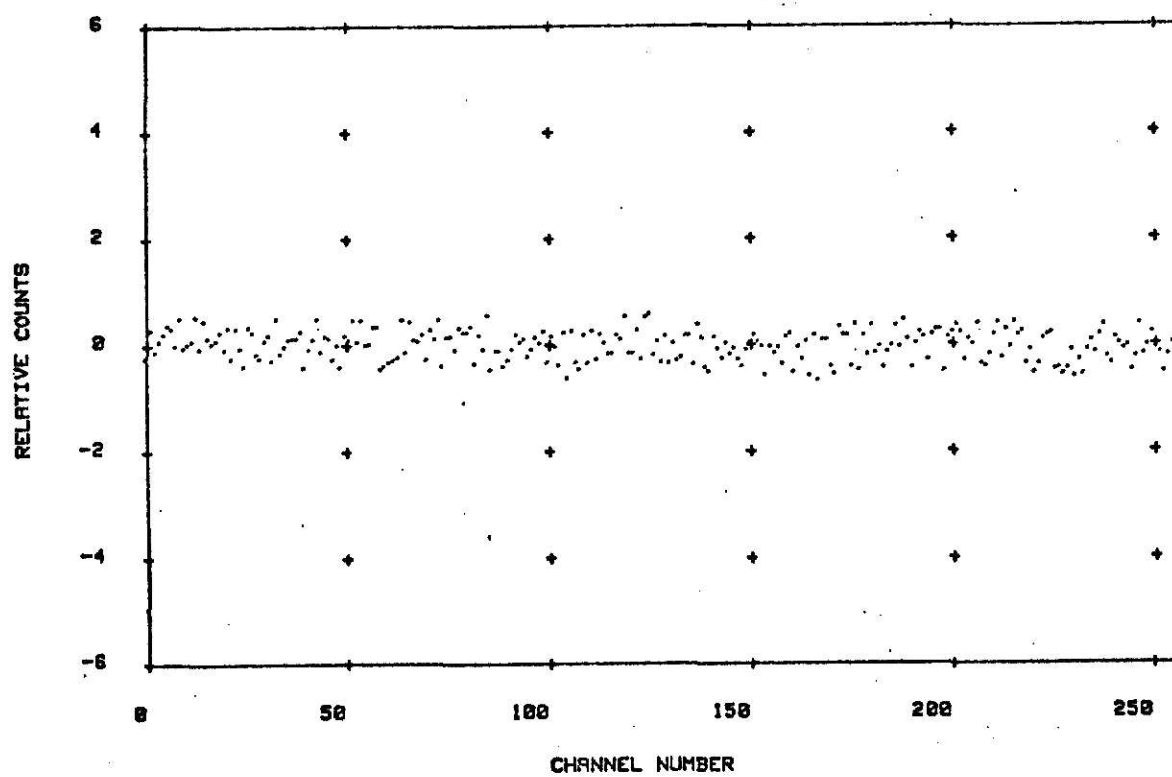


FIGURE 17e: Error After 7 Iterations

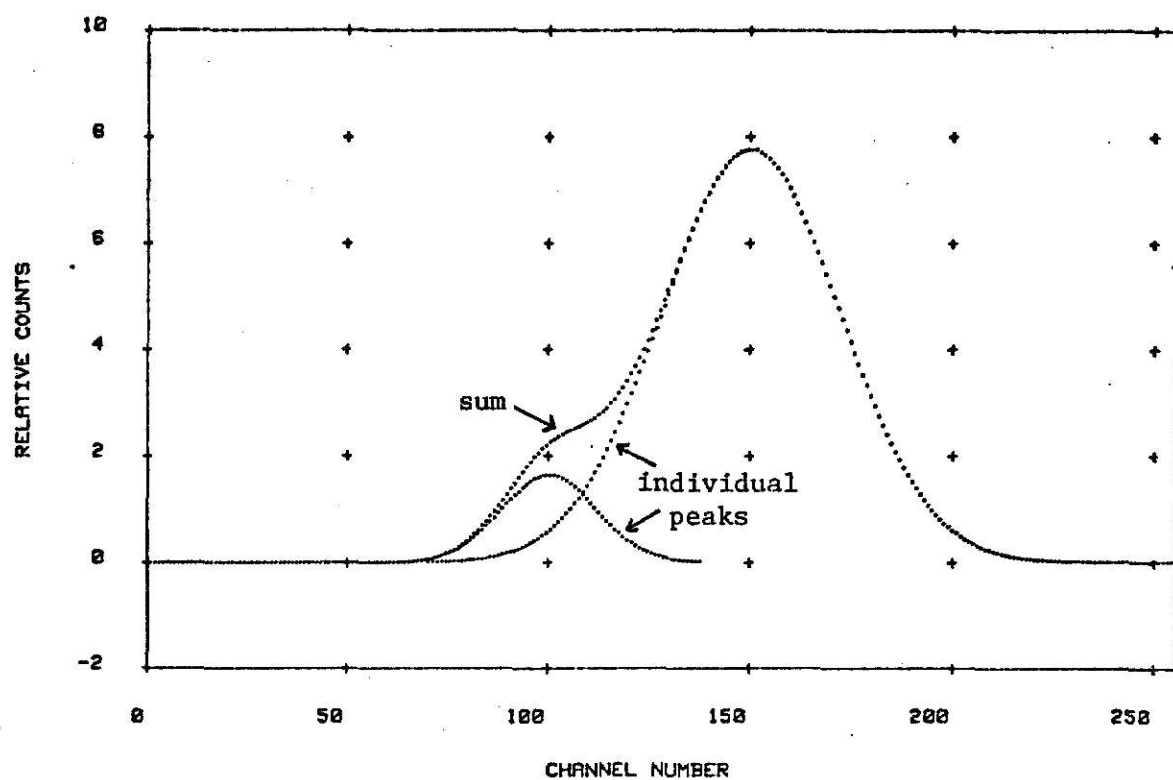


FIGURE 17f: Individual Peak Estimates and Sum After 7 Iterations

CHAPTER V
APPLICATION OF THE PEAK SEPARATION
ALGORITHM TO XRF SPECTRA

An X-ray fluorescence spectrum, such as that of 0.25% calcium in water as shown in Figure 7, is considerably more complicated than the simple Gaussian peaks previously considered. Primarily this is due to:

1. the presence of a significant background
2. the non-Gaussian peak shape
3. the presence of extraneous peaks

These are among the problems to be discussed in this chapter.

The spectra given in this section were acquired with the spectrum analyzer previously described. The excitation source was an Fe^{55} radioisotope which decays by electron capture to Mn^{55} resulting in the emission of manganese X-rays ($K\alpha = 5.9 \text{ KeV}$). The detector was a one inch diameter neon filled (1 atm.) proportional detector operated at a bias of 1300 volts. An Ortec Model 109PC preamp and an Ortec Model 570 main amplifier were used. Each of the resulting spectra was transferred to an Intel MDS-800 microcomputer development system and stored on diskette for later analysis.

Referring to the calcium spectrum in Figure 7, one notes three distinct peaks. The large high energy peak is referred to as the backscatter peak. It is a result of Compton scattering of the incident X-ray photon by outer shell electrons of the sample. Although the energy of the scattered photon is smaller than the incident photon, the energy loss is almost negligible in the energy range in which we are working, ranging from 0 to $\approx 2\%$ depending on the scattering angle.

The small peak just to the left of the backscatter (BKS) peak is due to fluorescence of the calcium in the sample. By forming the ratio of the fluorescence peak area to the BKS peak area, one eliminates or reduces effects of source decay, sample density changes, etc.

The broad peak at low energy is apparently a detector artifact. Judging from its energy, this peak appears to actually be the sum of Al and Ne fluorescence, both of which are materials present in the detector. This peak is present in every spectrum acquired.

Background Correction

A rather large background is noted in the XRF spectra. No explanation of the cause of this background is known, although it is assumed to arise in the detector. After a considerable amount of study of several spectra it was found to be roughly proportional to the size of the backscatter peak. Several background correction algorithms were investigated, with progressively better results:

1. A constant background, with height proportional to the area of the BKS peak in the low energy region was assumed. Then, a linearly decreasing background was assumed beginning at energy $P - W$ and continuing to zero at $P + W$, where P is the center of the BKS peak and W the width. Two sets of peak separation iterations were required, first to find the BKS peak parameters and then a second set after the background had been subtracted.
2. In the low energy region, the background height was proportional to the area under the BKS peak, as in case 1. The background then was gradually reduced to zero in the region of the BKS peak,

in proportion to the area under the BKS peak to the right (higher energy) of that point:

$$\text{BKG}(I) = K_1 \sum_{K=I}^{255} \text{BKS}(K) \quad (22)$$

where

$\text{BKG}(I)$ = background in channel I

$\text{BKS}(I) = D(I) \quad P-W < I < P+W$

and P and W refer to the position and width of the backscatter peak respectively. The constant K_1 was chosen to give the desired BKG height. Again, two sets of iterations were required.

3. The background equation was the same as in the previous case, but the calculation was actually done within the peak separation routine. The background array was added to the sum of the peak images in calculating the error array (12). This increased the execution speed, since only one set of iterations was required, and provided a more accurate calculation of the background.
4. The background correction was accomplished in the same manner as in case 3, but the area under the background rather than the height, was made proportional to the BKS peak area.

$$\text{BKG}(I) = K_2 \frac{\sum_{J=0}^{255} \text{BKS}(J) \cdot A(I)}{\sum_{J=0}^{255} A(J)} \quad (23)$$

$$\text{where } A(J) = \sum_{K=J}^{255} \text{BKS}(K)$$

and K_2 was chosen to give the required background height. This

method provides an insensitivity to gain shifts, solving a problem that was noted for case 3.

This last background correction algorithm is demonstrated in Figure 18 for a deionized water spectrum. Figure 18b shows the original data and the calculated background. A Gaussian image shape was used. The resulting individual peaks as well as the sum of the peaks plus background are given in Figure 18c. The difference between the peak sum and the original data is also shown (with same scale but vertically centered).

Non-Gaussian Peak Shapes

The technique employed in determining better peak shapes is demonstrated for the backscatter peak of a water spectrum in Figure 19. Four smaller overlapping Gaussian peaks were fit to the BKS peak. The small peak near channel number 98 was also fit to account for the small overlap of it with the BKS peak. The parameters of the four Gaussian peaks were then used to generate a combined BKS image which would fit the peak of the original data. The four Gaussian peaks were summed, normalized to position 128, to a height of 1.00 and to a width (10) of 37.23. The resulting image is given in Figure 20.

The same technique was employed to obtain the shapes of other peaks. The low energy peaks, presumed to be due to Ne and Al, were assigned to one combined peak in order to maximize run speed since the shape of the combined peak does not appear to change. Each element to be analyzed was assigned a peak image based on the results of a fit made on a relatively concentrated sample of the element so as to maximize the precision of the shape.

Results of the peak fit routine to the deionized water spectrum previously analyzed but with the improved peak images are given in Figure 21. A good fit has been obtained as seen from the error plot. The small mid-energy peak has been fit with a calcium image since it lies at the calcium fluorescence energy. Evidently this peak is the result of a small amount of calcium contamination in or on the detector (it was not eliminated by cleaning the detector surface).

Experimental Results

Analysis of a 0.25% calcium sample is demonstrated in Figure 22. Again, a relatively good fit has been obtained. The ratio of the calcium peak area to the BKS peak area, labeled "F2" near the bottom of the computer printout, is directly related to the elemental concentration. A series of six calcium samples, ranging from 0 to 1.0% calcium were analyzed and the calibration curve shown in Figure 23 was made. A linear regression analysis of the data points yielded a slope of 0.945 and an intercept of 0.001 with a correlation coefficient of 0.99999.

The analysis of titanium, demonstrated with a 0.25% sample in Figure 24, is more difficult because of the increased overlap between the photopeak and the BKS peak. A reasonably good fit has been obtained however, as can be seen from the error plot in Figure 24c. A calibration curve obtained from the analysis of a set of six samples ranging from 0 to 0.5% titanium is given in Figure 25. A slope of 1.596 and an intercept of 0.005 with a correlation coefficient of 0.9997 were obtained by linear regression.

As mentioned earlier in this chapter, these analyses were performed with an Fe^{55} X-ray source. With this source, elements ranging from sulfur through titanium, and possibly vanadium, can be analyzed. Elements outside

this range require a different X-ray source in order to provide adequate excitation efficiency. However, the techniques which have been discussed apply equally well to other exciters, resulting in a broad range of applicability.

SP028, DEION WATER, PURGED, 400 SEC., 9-6-79

PLOTTER SCALE FACTOR (COUNTS/DIV): 2000

IMG1, NORMALIZED GAUSSIAN IMAGE
FOR PEAK # 1 2

XRF BACKGROUND SUBTRACTION (3)
BACKSCATTER PEAK(S): 2
BACKGROUND CORRECTION FACTOR: 0.62

STARTING CHANNEL: 14

AREA = 935648.0

PASS # 0 REL STD ERROR (%) = 36.43533

LOW ENERGY BACKGROUND: 2325.427

P 1= 38.00000	H 1= 2000.000	W 1= 38.00000	A 1= 57631.40
P 2= 150.0000	H 2= 14000.00	W 2= 38.00000	A 2= 566353.3

PASS # 1 REL STD ERROR (%) = 20.16871

LOW ENERGY BACKGROUND: 2227.003

P 1= 31.36057	H 1= 1912.500	W 1= 27.57024	A 1= 52559.12
P 2= 153.0000	H 2= 13667.54	W 2= 38.03159	A 2= 553358.3

PASS # 2 REL STD ERROR (%) = 9.664601

LOW ENERGY BACKGROUND: 2201.999

P 1= 31.59896	H 1= 2028.258	W 1= 27.36258	A 1= 55551.10
P 2= 155.5584	H 2= 13759.57	W 2= 37.96735	A 2= 556035.8

PASS # 6 REL STD ERROR (%) = 9.534747

LOW ENERGY BACKGROUND: 2222.636

P 1= 31.42929	H 1= 2086.507	W 1= 27.37259	A 1= 57056.76
P 2= 155.6555	H 2= 13733.68	W 2= 38.41570	A 2= 561596.6

PASS # 7 REL STD ERROR (%) = 9.530070

LOW ENERGY BACKGROUND: 2222.160

P 1= 31.42194	H 1= 2093.323	W 1= 27.29124	A 1= 57102.22
P 2= 155.6580	H 2= 13725.34	W 2= 38.43134	A 2= 561484.7

PEAK TO BS PEAK AREA RATIOS:

F 1= .1016986

F 2= 1.000000

FIGURE 18a: Water XRF Spectrum

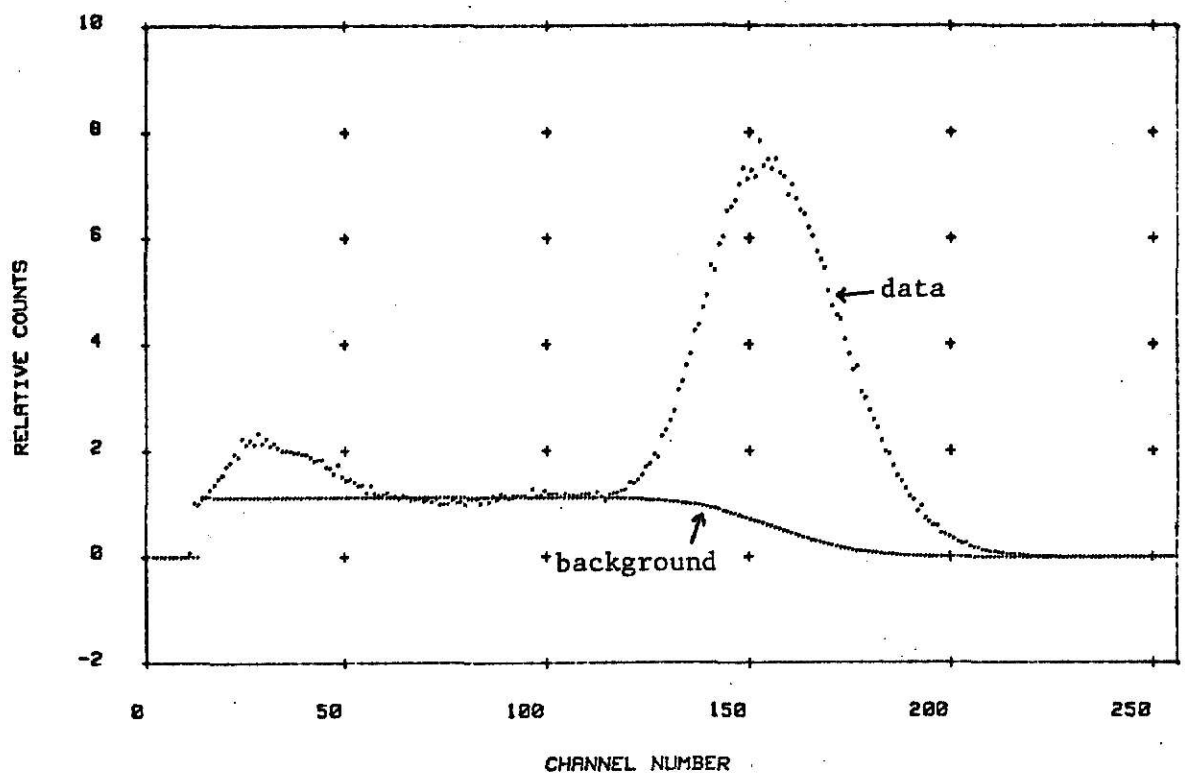


FIGURE 18b: Data and Calculated Background

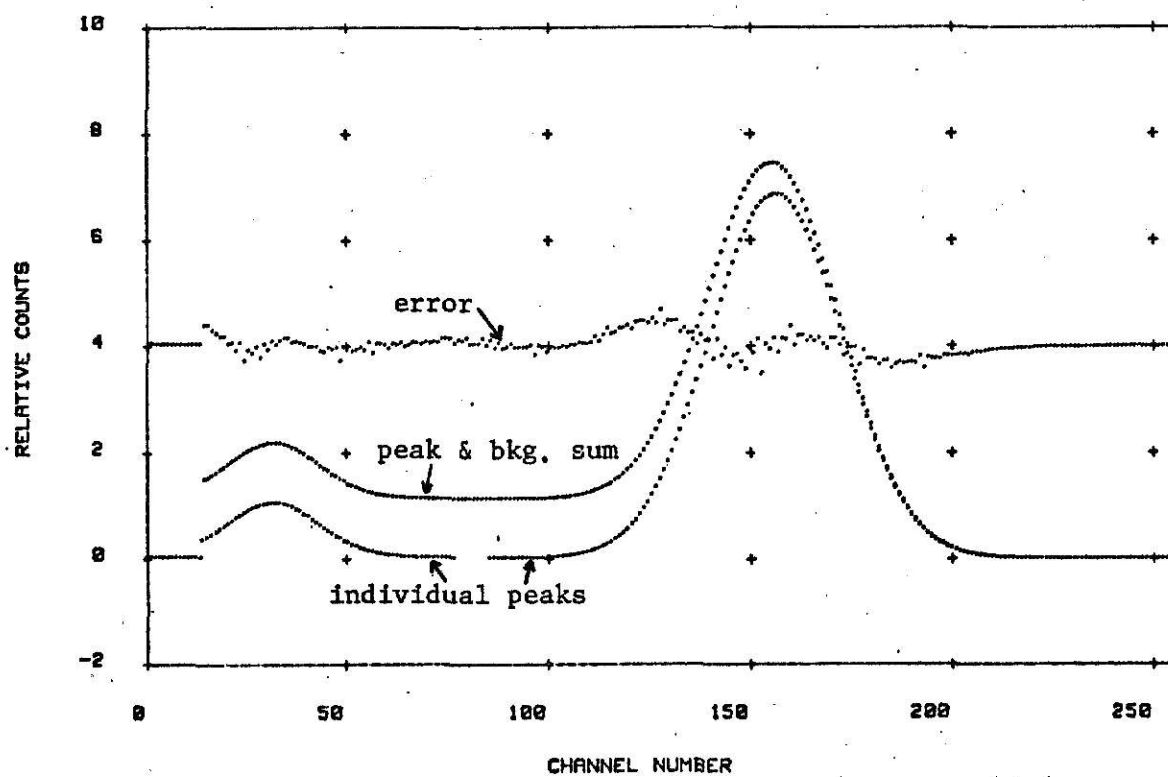


FIGURE 18c: Final Results

SP028, DEION WATER, PURGED, 400 SEC., 9-6-79

PLOTTER SCALE FACTOR (COUNTS/DIV): 2000

IMGL, NORMALIZED GAUSSIAN IMAGE
FOR PEAK # 1 2 3 4 5

XRF BACKGROUND SUBTRACTION (3)

BACKSCATTER PEAK(S): 2 3 4 5

BACKGROUND CORRECTION FACTOR: 0.58

STARTING CHANNEL: 70

AREA = 754239.9

PASS # 0 REL STD ERROR (%) = 30.81333

LOW ENERGY BACKGROUND: 1771.000

P 1= 95.00000	H 1= 300.0000	W 1= 30.00000	A 1= 9363.006
P 2= 135.0000	H 2= 1000.000	W 2= 20.00000	A 2= 21289.41
P 3= 154.0000	H 3= 10000.00	W 3= 35.00000	A 3= 372563.6
P 4= 170.0000	H 4= 2500.000	W 4= 25.00000	A 4= 66531.75
P 5= 185.0000	H 5= 1000.000	W 5= 20.00000	A 5= 21289.41

PASS # 14 REL STD ERROR (%) = 3.861882

LOW ENERGY BACKGROUND: 2065.730

P 1= 98.31875	H 1= 314.6284	W 1= 22.17982	A 1= 7419.993
P 2= 143.6506	H 2= 1402.250	W 2= 19.01058	A 2= 28375.28
P 3= 153.7255	H 3= 11548.47	W 3= 33.47951	A 3= 411562.0
P 4= 168.6070	H 4= 2746.645	W 4= 32.43072	A 4= 94818.00
P 5= 183.7339	H 5= 1013.774	W 5= 26.78624	A 5= 28905.80

PASS # 15 REL STD ERROR (%) = 3.855582

LOW ENERGY BACKGROUND: 2065.926

P 1= 98.30495	H 1= 315.2725	W 1= 22.06243	A 1= 7396.285
P 2= 143.7500	H 2= 1403.869	W 2= 18.97189	A 2= 28347.79
P 3= 153.6961	H 3= 11547.42	W 3= 33.48332	A 3= 411572.4
P 4= 168.6497	H 4= 2746.559	W 4= 32.32004	A 4= 94491.47
P 5= 183.6012	H 5= 1015.866	W 5= 27.08749	A 5= 29291.22

PEAK TO BS PEAK AREA RATIOS:

F 1= 1.312089E-02

F 2= 5.023852E-02

F 3= .7301229

F 4= .1676264

F 5= 5.196215E-02

FIGURE 19a: Peak Shape Determination on Water Spectrum

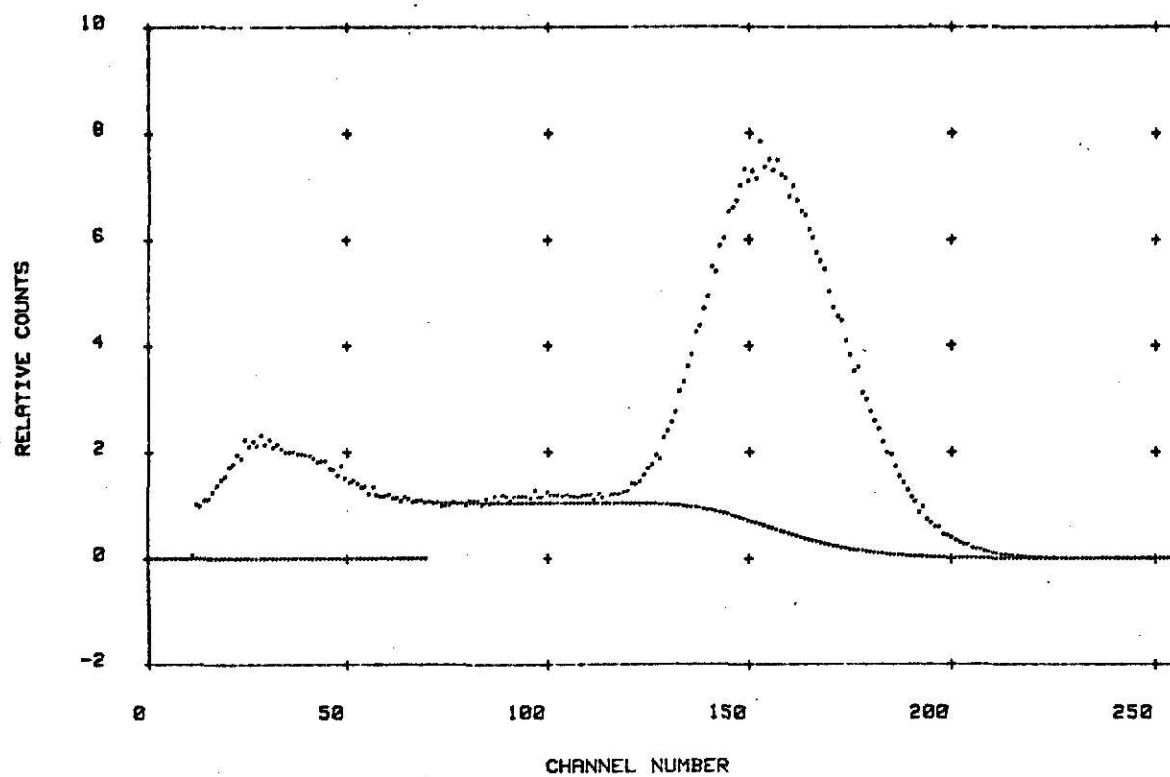


FIGURE 19b: Data and Background

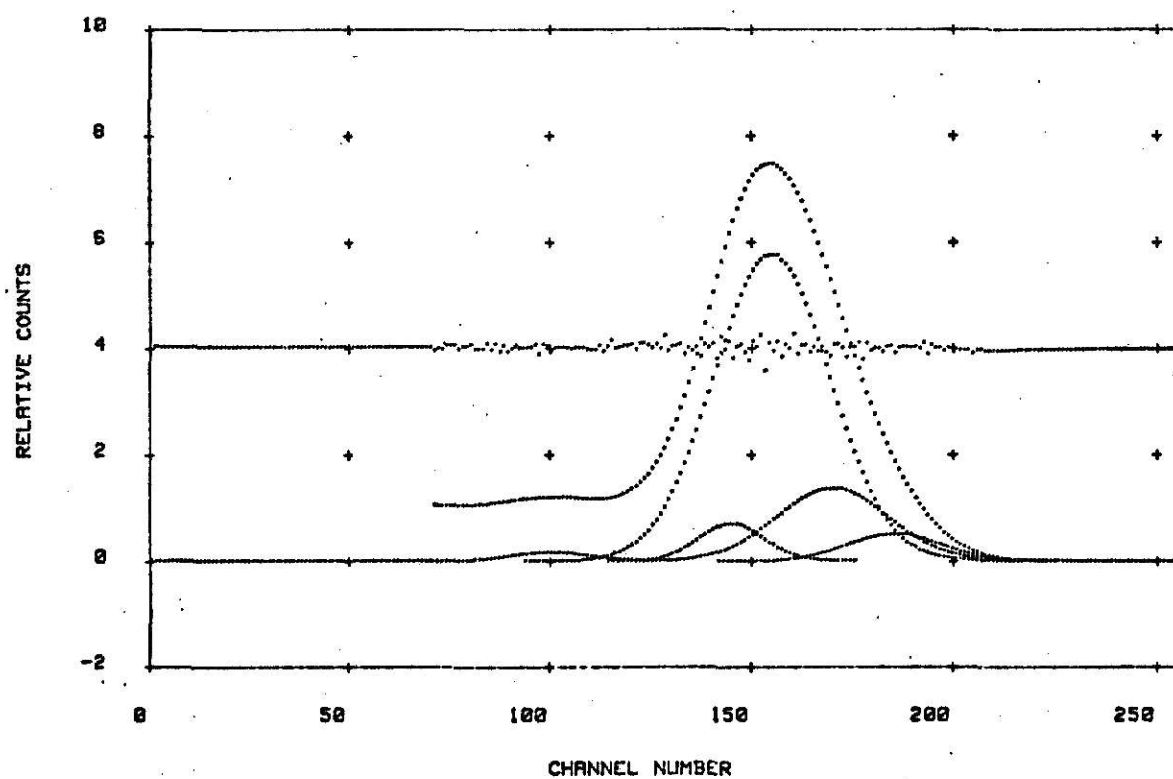


FIGURE 19c: Final Results

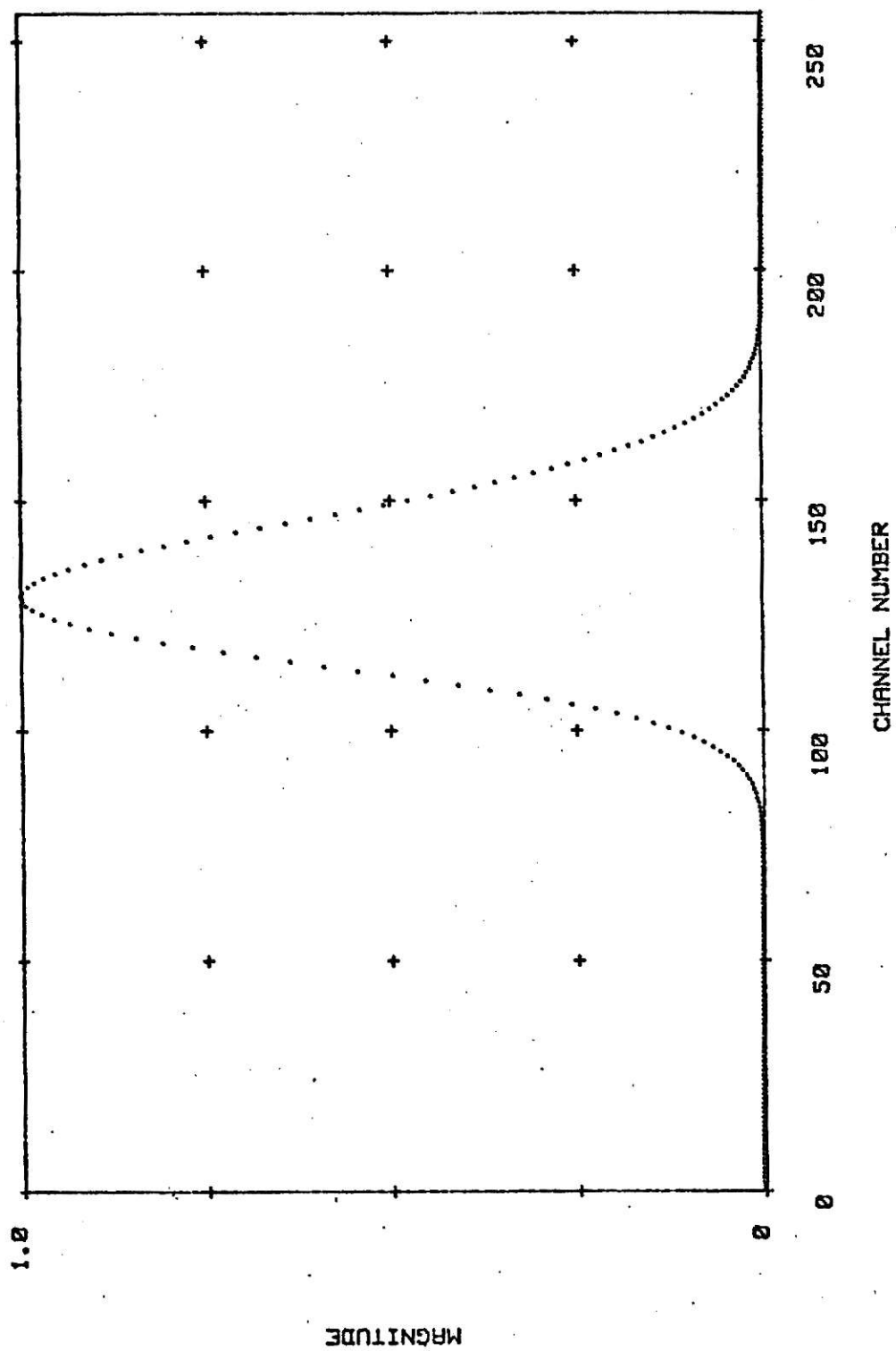


FIGURE 20: Manganese Backscatter Peak Image

PLOTTER SCALE FACTOR (COUNTS/DIV): 2000

IMGNE1, NE & AL IMAGE FROM SP018, NORMALIZED, 9-13-79
FOR PEAK # 1IMGCAL, CALCIUM IMAGE FROM SP020, NORMALIZED, 9-13-79
FOR PEAK # 2IMGMN2, MANGANESE PEAK FROM WATER SAMPLE
FOR PEAK # 3

XRF BACKGROUND SUBTRACTION (3)

BACKSCATTER PEAK(S): 3

BACKGROUND CORRECTION FACTOR: 0.58

STARTING CHANNEL: 14

AREA = 935648.0

PASS # 0 REL STD ERROR (%) = 28.66238

LOW ENERGY BACKGROUND: 2288.592

P 1= 32.00000	H 1= 2500.000	W 1= 30.00000	A 1= 74897.99
P 2= 100.0000	H 2= 500.0000	W 2= 30.00000	A 2= 16063.78
P 3= 158.0000	H 3= 15000.00	W 3= 40.00000	A 3= 639645.8

PASS # 1 REL STD ERROR (%) = 7.631659

LOW ENERGY BACKGROUND: 2131.853

P 1= 29.00000	H 1= 2212.947	W 1= 30.31684	A 1= 66625.14
P 2= 98.82859	H 2= 350.0000	W 2= 25.19315	A 2= 9442.854
P 3= 155.0000	H 3= 13663.31	W 3= 40.15164	A 3= 584855.0

PASS # 6 REL STD ERROR (%) = 3.467705

LOW ENERGY BACKGROUND: 2061.710

P 1= 27.67066	H 1= 2362.437	W 1= 27.54867	A 1= 64650.13
P 2= 97.97045	H 2= 326.0550	W 2= 21.69005	A 2= 7573.664
P 3= 154.2869	H 3= 13684.62	W 3= 38.56532	A 3= 562635.3

PASS # 7 REL STD ERROR (%) = 3.447111

LOW ENERGY BACKGROUND: 2062.175

P 1= 27.61182	H 1= 2367.506	W 1= 27.46510	A 1= 64587.87
P 2= 97.71793	H 2= 325.8954	W 2= 21.76015	A 2= 7594.417
P 3= 154.2813	H 3= 13700.63	W 3= 38.52673	A 3= 562730.7

PEAK TO BS PEAK AREA RATIOS:

F 1= .1147758

F 2= 1.349565E-02

F 3= 1.000000

FIGURE 21a: Water Spectrum Analysis With Non-Gaussian Peak Shapes

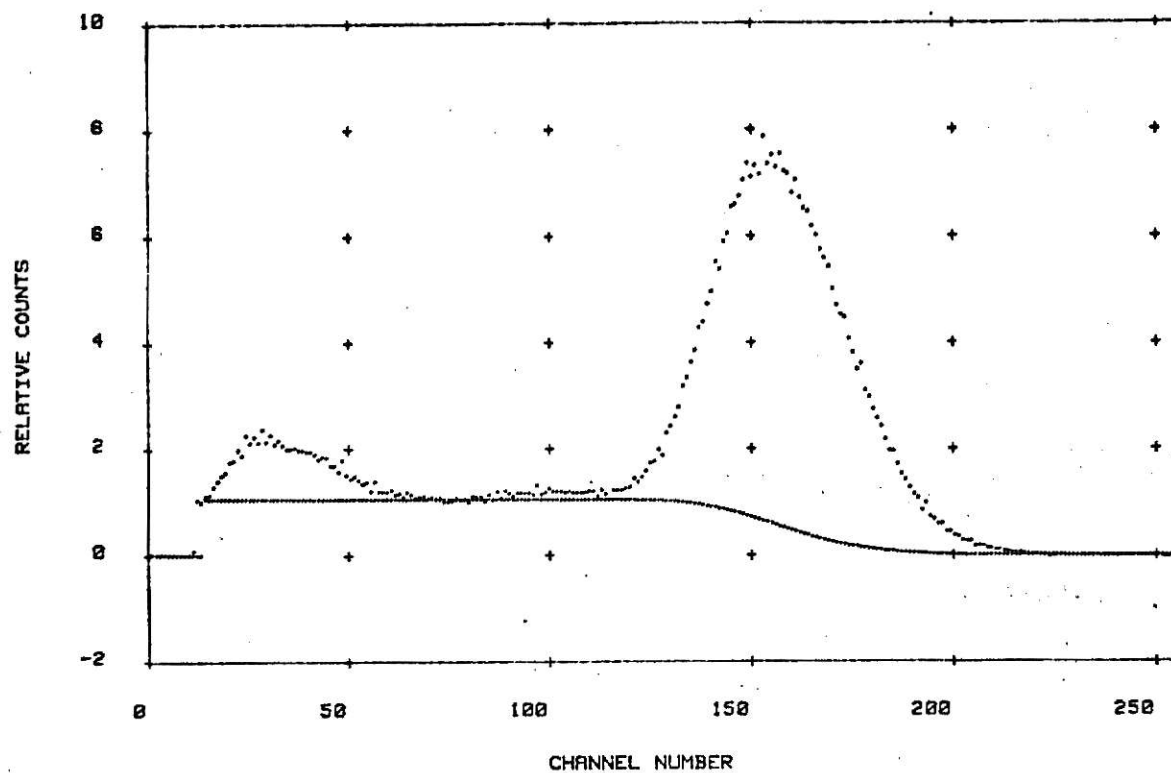


FIGURE 21b: Data and Background

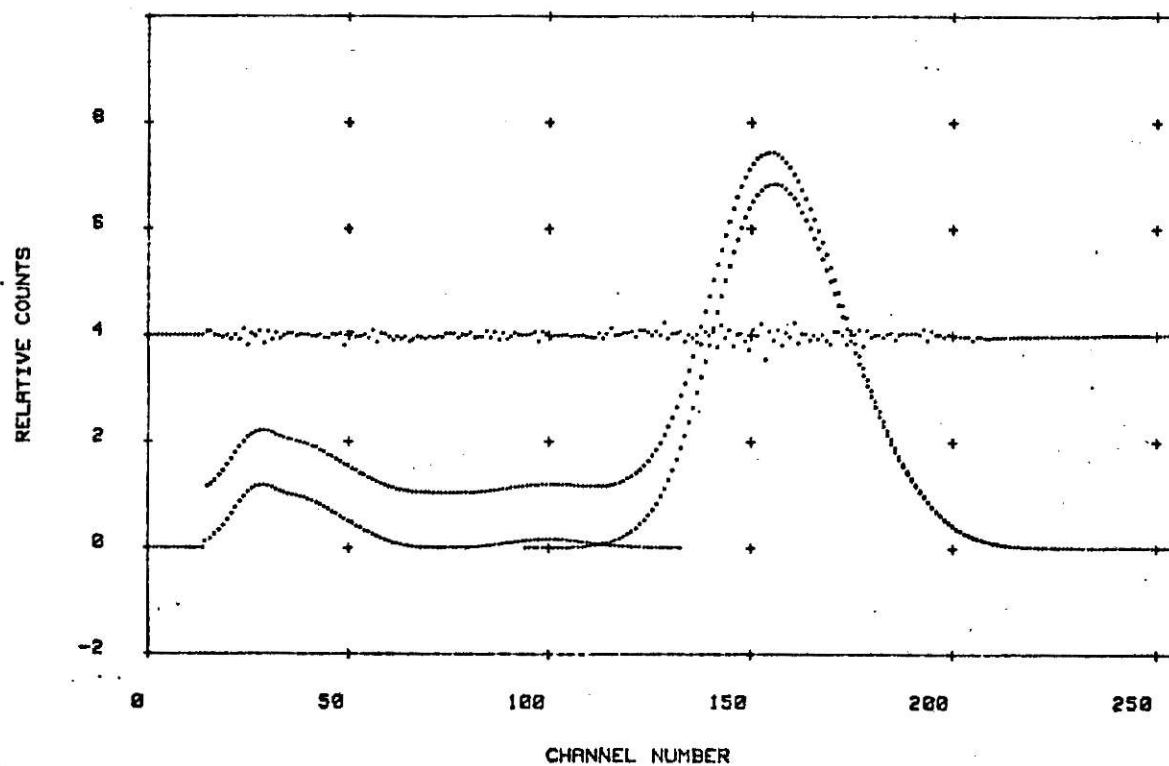


FIGURE 21c: Results

SP027, 0.25% CALCIUM, PURGED, 400 SEC., 9-6-79

PLOTTER SCALE FACTOR (COUNTS/DIV): 2000

IMG01, NE & AL IMAGE FROM SP018, NORMALIZED, 9-13-79
FOR PEAK # 1

IMG01, CALCIUM IMAGE FROM SP020, NORMALIZED, 9-13-79
FOR PEAK # 2

IMG012, MANGANESE PEAK FROM WATER SAMPLE
FOR PEAK # 3

XRF BACKGROUND SUBTRACTION (3)

BACKSCATTER PEAK(S): 3

BACKGROUND CORRECTION FACTOR: 0.58

STARTING CHANNEL: 14

AREA = 1077272.

PASS # 0 REL STD ERROR (%) = 17.65429

LOW ENERGY BACKGROUND: 2331.745

P 1= 30.00000	H 1= 2500.000	W 1= 30.00000	A 1= 74693.40
P 2= 100.0000	H 2= 5000.000	W 2= 30.00000	A 2= 160637.8
P 3= 155.0000	H 3= 15000.00	W 3= 40.00000	A 3= 639645.8

PASS # 1 REL STD ERROR (%) = 4.707627

LOW ENERGY BACKGROUND: 2116.193

P 1= 27.63098	H 1= 2299.655	W 1= 29.59377	A 1= 67341.48
P 2= 99.22603	H 2= 4347.675	W 2= 28.23628	A 2= 131468.0
P 3= 154.3097	H 3= 13734.53	W 3= 39.46400	A 3= 577845.0

PASS # 6 REL STD ERROR (%) = 3.517438

LOW ENERGY BACKGROUND: 2076.554

P 1= 28.08210	H 1= 2499.368	W 1= 29.60397	A 1= 73344.14
P 2= 99.47451	H 2= 4676.317	W 2= 27.42970	A 2= 137366.4
P 3= 154.1702	H 3= 13667.36	W 3= 38.87027	A 3= 566355.4

PASS # 7 REL STD ERROR (%) = 3.511320

LOW ENERGY BACKGROUND: 2076.838

P 1= 28.07183	H 1= 2498.708	W 1= 29.61765	A 1= 73354.24
P 2= 99.46930	H 2= 4681.445	W 2= 27.40616	A 2= 137399.1
P 3= 154.1677	H 3= 13673.72	W 3= 38.85671	A 3= 566421.6

PEAK TO BS PEAK AREA RATIOS:

F 1= .1295047

F 2= .2425739

F 3= 1.000000

FIGURE 22a: Spectrum of 0.25% Calcium

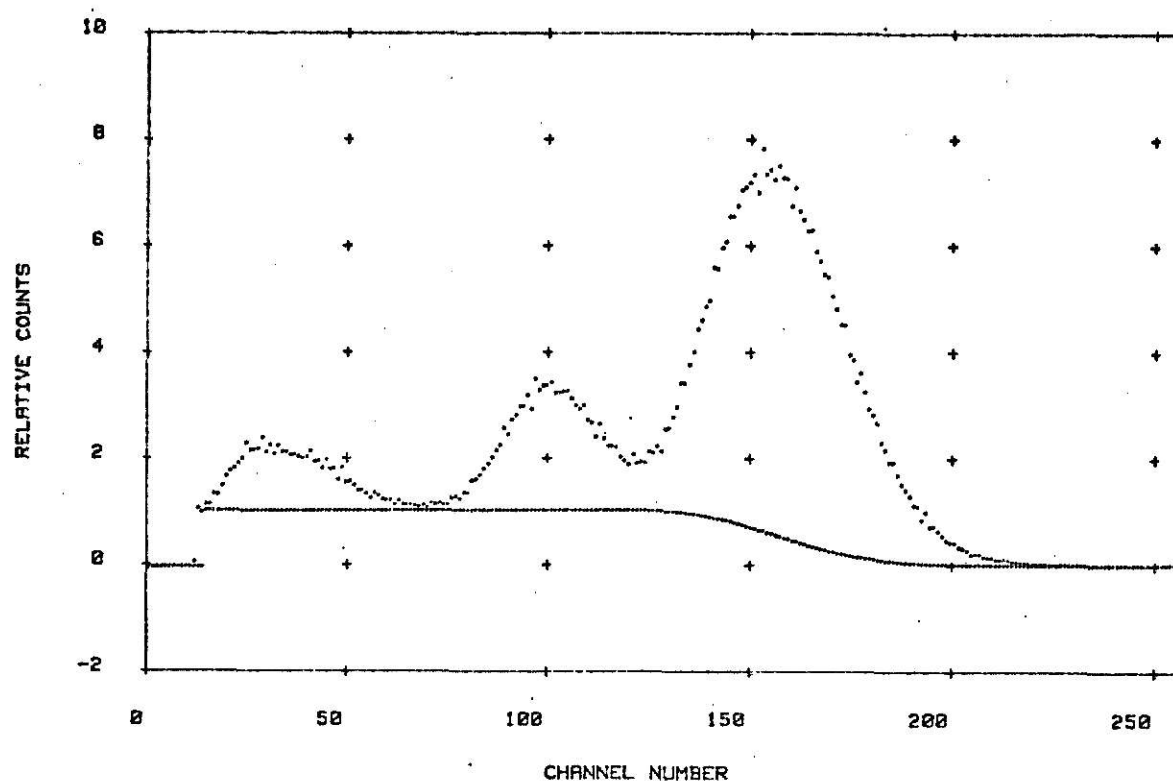


FIGURE 22b: Data and Background

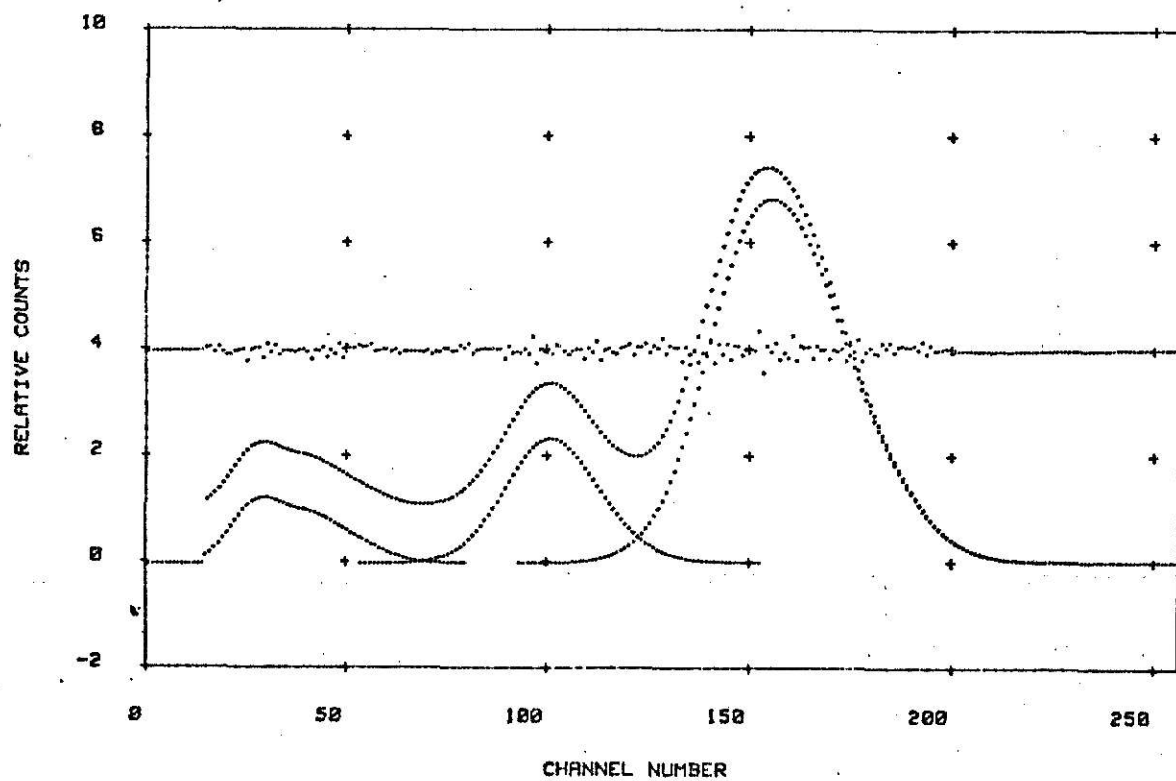


FIGURE 22c: Results

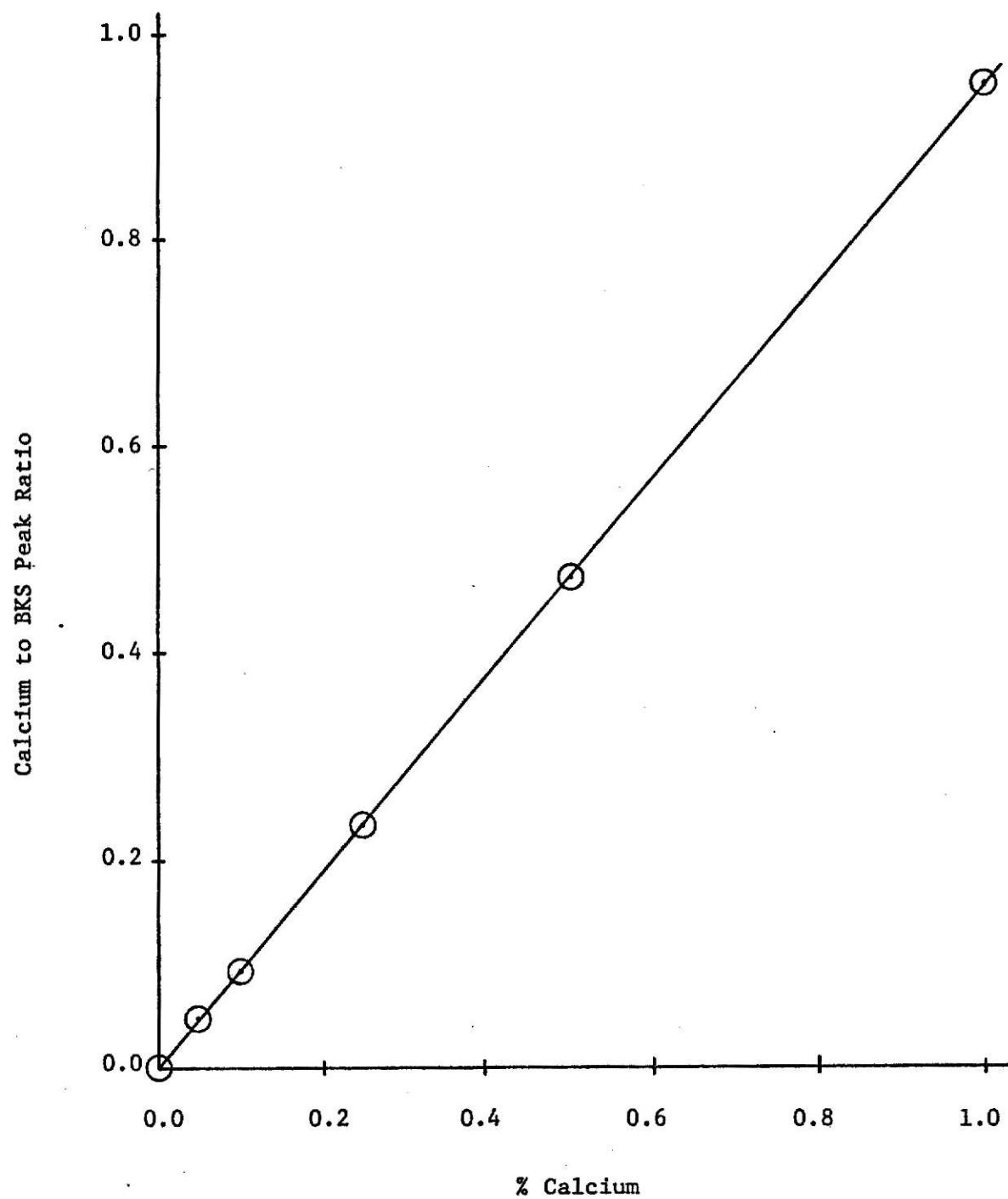


FIGURE 23: Calcium Calibration Curve

SP038, 0.25% TITANIUM, PURGED, 400 SEC, 9-7-79

PLOTTER SCALE FACTOR (COUNTS/DIV): 2000

IMGNE1, NE & AL IMAGE FROM SP018, NORMALIZED, 9-13-79
FOR PEAK # 1

IMGT11, TITANIUM IMAGE FROM SP034, NORMALIZED, 9-13-79
FOR PEAK # 2

IMGPN2, MANGANESE PEAK FROM WATER SAMPLE
FOR PEAK # 3

XRF BACKGROUND SUBTRACTION (3)

BACKSCATTER PEAK(S): 3

BACKGROUND CORRECTION FACTOR: 0.58

STARTING CHANNEL: 14

AREA = 1141917.

PASS # 0 REL STD ERROR (%) = 16.35426

LOW ENERGY BACKGROUND: 1921.893

P 1= 30.00000	H 1= 2500.000	W 1= 30.00000	A 1= 74693.40
P 2= 125.0000	H 2= 5000.000	W 2= 30.00000	A 2= 154970.6
P 3= 155.0000	H 3= 13000.00	W 3= 30.00000	A 3= 526695.9

PASS # 1 REL STD ERROR (%) = 6.890608

LOW ENERGY BACKGROUND: 2032.611

P 1= 28.73688	H 1= 2690.921	W 1= 30.87965	A 1= 82375.45
P 2= 122.5369	H 2= 6273.858	W 2= 33.80534	A 2= 219118.1
P 3= 154.2689	H 3= 13584.38	W 3= 38.29160	A 3= 554555.8

PASS # 6 REL STD ERROR (%) = 4.254377

LOW ENERGY BACKGROUND: 1983.746

P 1= 28.43179	H 1= 2583.539	W 1= 31.93428	A 1= 81532.58
P 2= 121.2929	H 2= 6089.387	W 2= 35.38231	A 2= 222598.0
P 3= 154.7311	H 3= 13524.81	W 3= 37.63498	A 3= 542629.9

PASS # 7 REL STD ERROR (%) = 4.254135

LOW ENERGY BACKGROUND: 1983.153

P 1= 28.45253	H 1= 2580.220	W 1= 32.01218	A 1= 81620.67
P 2= 121.3074	H 2= 6086.259	W 2= 35.41855	A 2= 222711.6
P 3= 154.7351	H 3= 13523.65	W 3= 37.62760	A 3= 542477.8

PEAK TO BS PEAK AREA RATIOS:

F 1= .1504590

F 2= .4185451

F 3= 1.000000

FIGURE 24a: Spectrum of 0.25% Titanium

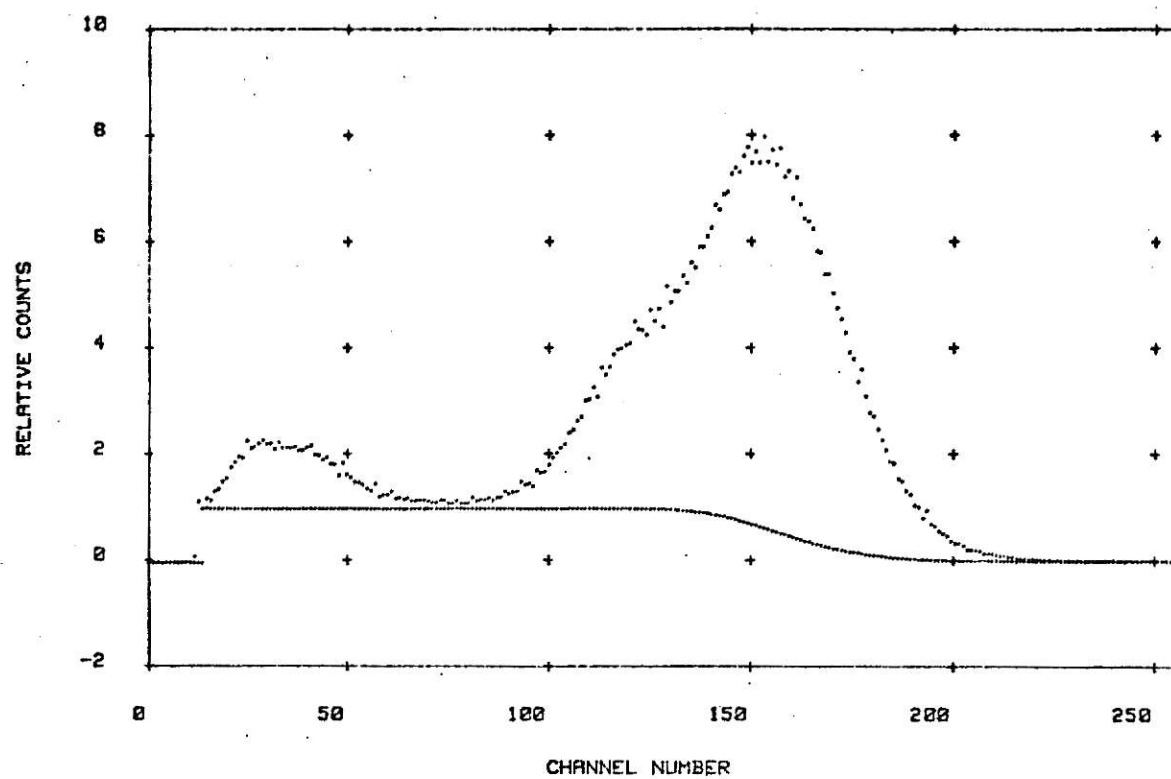


FIGURE 24b: Data and Background

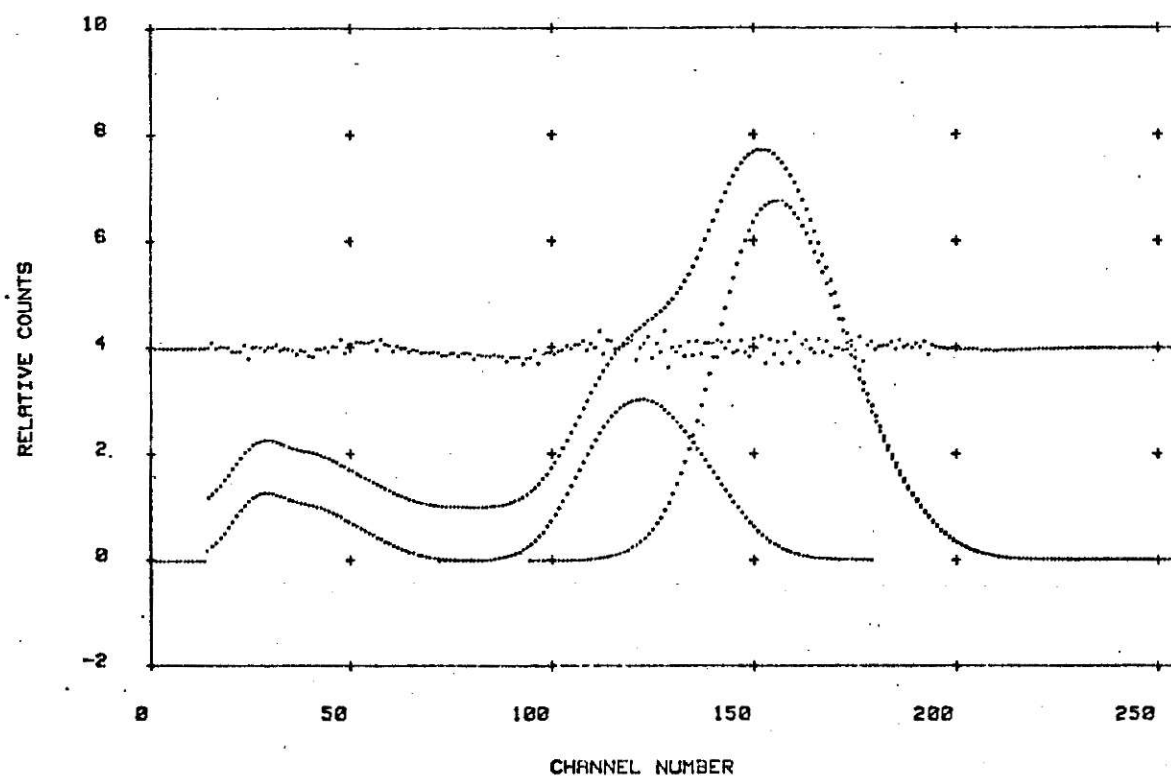


FIGURE 24c: Results

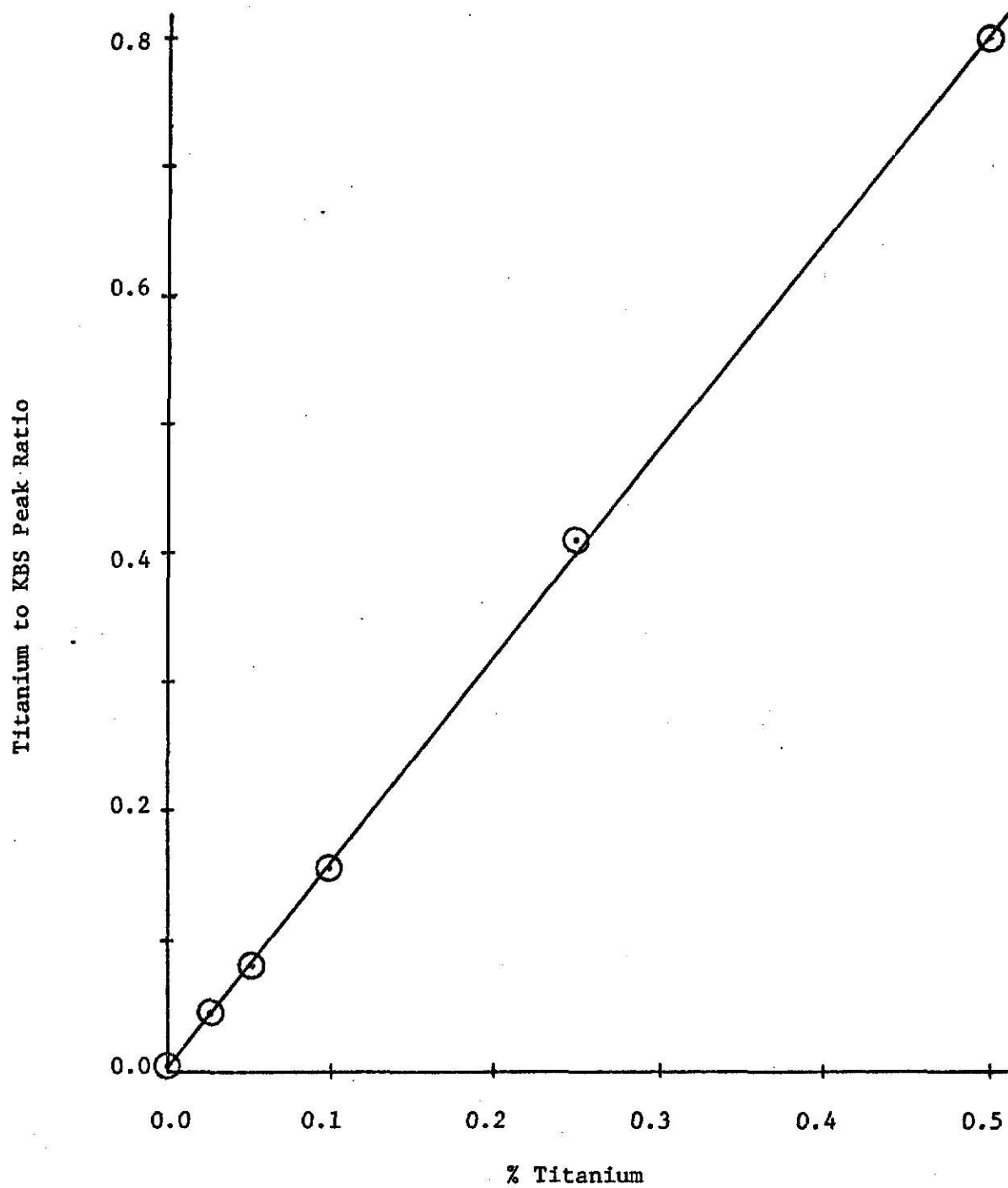


FIGURE 25: Titanium Calibration Curve

CHAPTER VI

CONCLUSIONS

This report has described the development of an X-ray fluorescence spectrometer. Because of its intended use in a chemical processing plant, some design compromises had to be made. For example, optimum detector resolution was sacrificed in order to gain the required reliability and operational simplicity.

After a brief introduction to the physics of X-ray fluorescence, common instrumental techniques were discussed. The electronic hardware, designed around two microcomputers, was then described. The use of microcomputers has contributed significantly to this instrument.

A major part of this report has been devoted to a computational method of determining the areas under the fluorescence spectrum peaks. The algorithm was described, and its operation was demonstrated on computer generated data. Application of the technique to actual X-ray fluorescence data was then presented and special requirements were described. Experimental results are given for analysis of the elements calcium and titanium. A dramatic improvement in detectability, especially for the titanium analysis, has been achieved.

CHAPTER VII

REFERENCES

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DEVELOPMENT OF AN X-RAY FLUORESCENCE
SPECTROMETER WITH PEAK SEPARATION SOFTWARE
FOR IMPROVED RESOLUTION

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AN ABSTRACT OF A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Electrical Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1980

ABSTRACT

The development of an x-ray fluorescence spectrometer for use in a chemical processing plant is described. The design emphasizes detector reliability and operational simplicity. A significant feature of the approach taken is the use of microprocessor hardware to implement a computational algorithm for distinguishing between the various energy peaks produced by the sample being analyzed. Experimental results are given which show a dramatic improvement in detectability.