

Presented at the 6th Workshop on RF Superconductivity
October 4-8, 1993, CEBAF, Newport News, Virginia

Hydrogen Contamination of Niobium Surfaces

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INTRODUCTION

The presence of hydrogen is blamed for dramatic reductions in cavity Q's.¹⁻⁷ Hydrogen concentration is difficult to measure, so there is a great deal of Fear, Uncertainty, and Doubt (FUD) associated with the problem. This paper presents measurements of hydrogen concentration depth profiles, commenting on the pitfalls of the methods used and exploring how material handling can change the amount of hydrogen in pieces of niobium.

Hydrogen analysis was performed⁸ by a forward scattering experiment with Helium used as the primary beam.⁹ This technique is variously known as FRES (Forward Recoil Elastic Scattering), FRS, HFS (Hydrogen Forward Scattering), and HRA (Hydrogen Recoil Analysis). Some measurements were also made using SIMS (Secondary Ion Mass Spectrometry).

Both HFS and SIMS are capable of measuring a depth profile of Hydrogen. The primary difficulty in interpreting the results from these techniques is the presence of a surface peak which is due (at least in part) to contamination with either water or hydrocarbons.

With HFS, the depth resolution is about 30 nm, and the maximum depth profiled is about 300 nm. (This 10-1 ratio is unusually low for ion beam techniques, and is a consequence of the compromises that must be made in the geometry of the experiment, surface roughness, and energy straggling in the absorber foil that must be used to filter out the forward scattered helium.)

All the observed HFS spectra include a "surface peak" which includes both surface contamination and any real hydrogen uptake by the niobium surface. Some contamination occurs during the analysis. The vacuum in the analysis chamber is typically a few times 10^{-6} torr, and some of the contamination is in the form of hydrocarbons from the pumping system. Hydrocarbons normally form a very thin (less than a monolayer) film which is in equilibrium between arrival rate and the evaporation rate. In the presence of the incoming ion beam, however, these hydrocarbons crack on the surface into non-volatile components. Equilibrium is lost, and the surface builds up a layer of carbon-based gunk.

A key question in this analysis is what depth scale is involved in the environmental contamination. The diffusion constant of dissolved hydrogen (in the α -Nb phase) at room temperature is quite high, making it unlikely that significant non-uniformities will be observed in that part of the sample. On the other hand, the surface of niobium, after treatment and exposure to air is known to have other phases present, primarily oxides. Hydrogen content in these other phases will be different from that in the α phase, even under equilibrium conditions. Furthermore, the diffusion coefficient of hydrogen in an oxide phase is lower than that in metals. Finally, hydrogen and stress are known to interact in niobium; this is relevant because the surface layer of mechanically worked (rolled) samples is typically highly stressed.

In some of the discussions below, we will use the concept of "bulk" concentration - this is a codeword for the top 200 nm, not counting surface contamination. This is both the region that is sampled by HFS, and is the relevant region for determining RF properties because the penetration depth for 1.5 GHz RF fields in niobium is about 36 nm.

EXPERIMENTAL PROCEDURE

The samples, 1 cm \times 1 cm \times 0.15 cm in size, were cut from reactor grade (RRR=40) and high purity (RRR=250) sheets of niobium. Surface roughnesses of about 1 μ m rms (reactor grade) and 0.14 μ m rms (high purity) were measured by stylus techniques on the unprocessed samples. The surface treatments applied to the various pieces were selected as being typical for the preparation of superconducting cavities. Table 1 summarizes which samples received which treatments, using the shorthand description elaborated below.

As-received: The samples were degreased, rinsed with DI (deionized) water, and cleaned with reagent grade methanol.

BCP: Chemical polishing is done in a buffered solution of equal parts of hydrofluoric (49%), nitric(70%) and phosphoric (85%) acids. After the polishing operation, the sample is rinsed in DI water and in methanol.

CP: Chemical polishing is done in a solution of 40% hydrofluoric acid (40%), and 60% nitric acid (70%). After the polishing operation, the sample is rinsed in DI water and in methanol.

Anodized 100V: Anodic oxidation is carried out in a diluted ammonium hydroxide solution (10%) at a voltage of 100V. Based on anodization conditions, the thickness of the Nb₂O₅ layer should be about 200 nm.⁴

HT 800°C: Heat treatment is performed at 800°C for 5 hours at 3×10^{-6} to 7×10^{-7} torr in a vacuum furnace with a base pressure of 2×10^{-7} torr. Nitrogen gas is introduced into the furnace prior to the unloading operation.

HT 800°C/Ti: The niobium sample is placed inside a titanium box and the heat treatment is performed as above.

260°C/5h: The anodized sample is baked at 260°C for 5 hours at a pressure of a few $\times 10^{-7}$ torr.

EBW: electron beam welding is performed on the niobium sample in the CEBAF EBW machine at a pressure of about 5×10^{-5} torr.

RESULTS AND DISCUSSION

With a few notable exceptions, all HFS data showed a strong surface peak, representing approximately 11×10^{15} atoms/cm² of hydrogen. The depth resolution of the technique makes it impossible to accurately determine the concentration or thickness of this layer, but it is no more than 60 nm thick with a concentration of at least 4 at%.

The surface peak is due at least in part to water uptake and/or hydrocarbon deposition during the experiment, as discussed above. The expected size of this peak was computed based on the dose of analyzing beam and a calibration run on a clean silicon wafer. The surface peak size shown in table 1 is given both raw and (in parentheses) after correction for this effect.

Individual HFS spectra are shown as figures 1 through 12. Sample number 1, which was unprocessed Reactor Grade material, showed much more hydrogen content in its bulk than any of the other samples (between 3.5 and 4.9 at%), even a piece from the same batch that was BCP cleaned removing 90 μm of material. An obvious conclusion is that the material contains (after rolling) a damaged, hydrogen rich layer between 0.25 μm and 90 μm thick.

All of the other non-anodized samples showed between 0.25 and 0.57 at% hydrogen content in the bulk. This is near the detectability limit for HFS, but is clearly a real signal. The anodized samples both showed a clear dip in the top 200 nm zone, indicating that the hydrogen concentration in the oxide is smaller than the metallic niobium.

The differences in "bulk" concentration among the remaining samples is relatively small. The highest readings (0.46 to 0.57 at%) were observed near the surface in the high purity niobium before any chemistry was performed at CEBAF, and in one such sample which received BCP but was not heat treated. The remaining results were all clustered in the

0.25 to 0.37 at% range. This included both CP samples and BCP samples, heat treated and not.

One more anomaly was the additional surface hydrogen content of the EBW sample.

The anticipated reduction in hydrogen content after heat treatment, paralleling improvement in Q-disease reported in other laboratories,⁷ was weak at best. Comparisons of sample sets 14, 15 and 16 show a reduction in hydrogen content of 20% to 50%.

Another reported effect is an increase in Q-disease when the temperature of BCP is increased.⁷ Samples 14, 23 and 24 seem to support the argument that hydrogen content is increased under these conditions, although again the quantitative changes are small.

A comparison of samples 19 and 18 shows the influence of baking (at 260°C) an anodized sample. There is some evidence that hydrogen diffuses into the bulk.

SIMS gives bulk results at least approximately consistent with HFS, although SIMS is notoriously hard to calibrate. Figure 13 gives hydrogen concentration in the 0.02 at% range for BCP'd high RRR niobium (similar to sample 14). Figure 14 gives hydrogen concentration in the 0.04 at% range for a section of EBW niobium (similar to sample 22).

Our results mostly parallel those of Antoine *et al.*¹⁰

CONCLUSIONS

Hydrogen forward scattering can be used as a probe of hydrogen concentration in niobium. It is adequately sensitive and examines the relevant depth scale for RF properties. More work needs to be done to improve its reliability, however, especially in regards to the interpretation of the surface peak. By itself, it is insufficient to make sense of the surface chemistry. Additional techniques need to be employed. The key piece of information missing at this point is a (diffraction-based) technique that can identify crystallographic phases in the material as a function of temperature.

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TABLE I. Hydrogen depth profile of niobium samples

Sample No	Treatment	Surface rms(μm)	0-500Å at %	500-1000Å at %	1000-2500Å at %	HFS Fig.No.
1	Reactor grade-as received	1.09	7.7 (4.3)	4.9	3.5	1
2	Reactor grade-BCP (90 μm)	1.24	4.4 (1.0)	0.32	0.30	2
13	RRR-as received	0.14	4.8 (1.4)	0.57	0.37	3
14	RRR-BCP(90 μm)	0.58	4.4 (1.0)	0.46	0.33	4
15	RRR-BCP(90 μm)-HT 800°C	0.83	3.3 (0.0)	0.27	0.27	5
16	RRR-BCP(90 μm)-HT 800°C/Ti	0.66	3.7 (0.3)	0.25	0.25	6
17	RRR-BCP(90 μm)-HT 800°C/Ti-BCP(1mn)	1.03	4.0 (0.6)	0.29	0.25	7
23	RRR-CP at 23°C (90 μm)	0.66	4.0 (0.9)	0.33	0.33	8
24	RRR-CP at 28°C (95 μm)	0.46	5.2 (1.8)	0.36	0.36	9
22	RRR-EBW	-----	10.0 (6.9)	0.33	0.33	10

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TABLE II. Hydrogen depth profile of anodized niobium samples

Sample No	Treatment	Surface rms(μm)	0-740Å at %	740-1150Å at %	1150-2240Å at %	>2240Å at %	HFS Fig.No
19	RRR-BCP(90 μm)-anodized 100V	0.90	4.7 (2.3)	0.40	0.09	0.15	11
18	RRR-BCP(90 μm)-anodized 100V- 260°C/ 5 hours	0.88	4.4 (2.0)	0.58	0.18	0.30	12

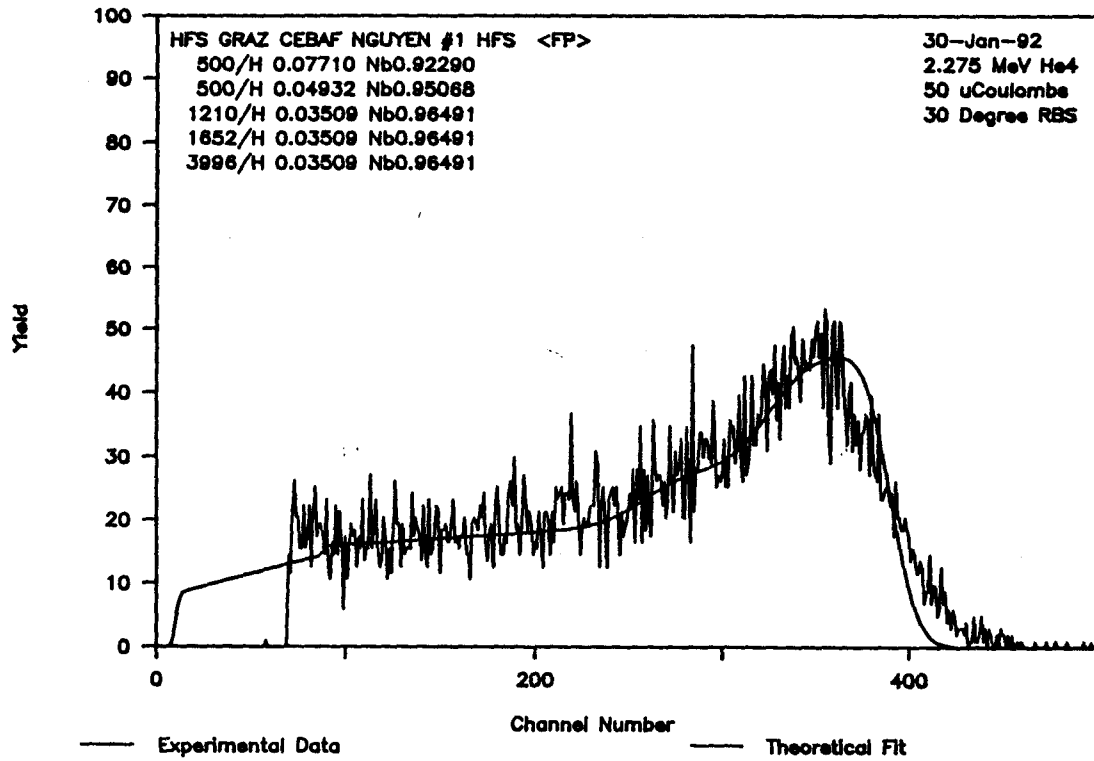


Figure 1. Reactor grade - as received

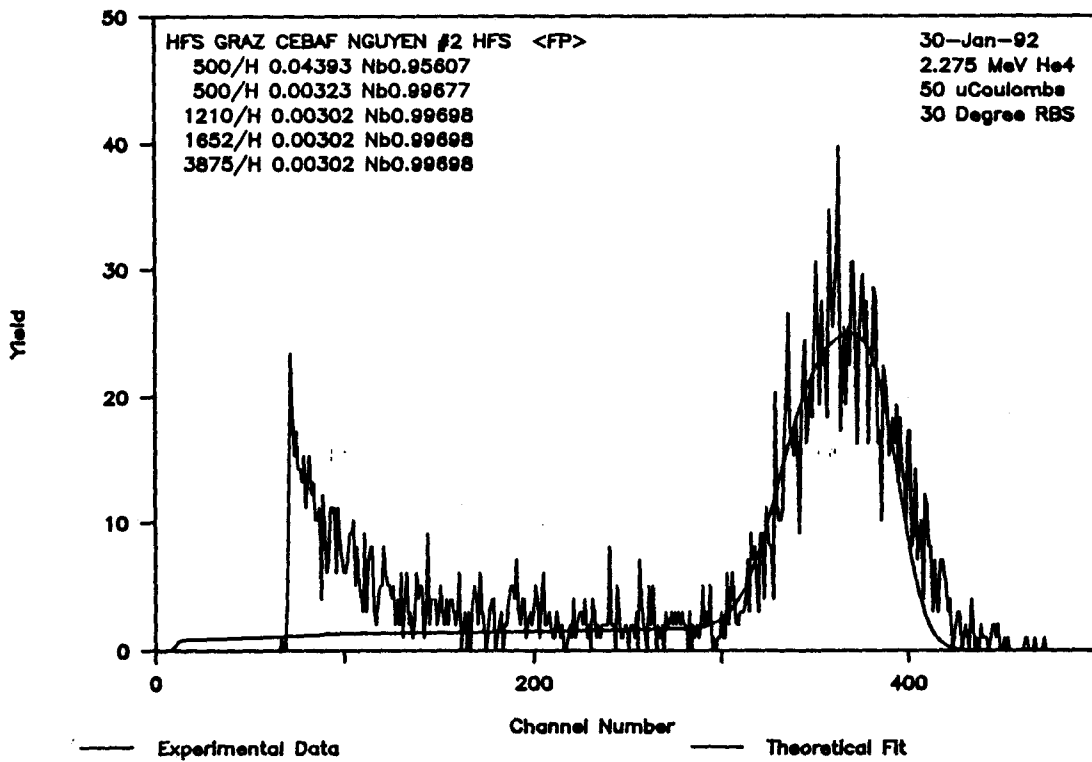


Figure 2. Reactor grade - BCP (90 μ m)

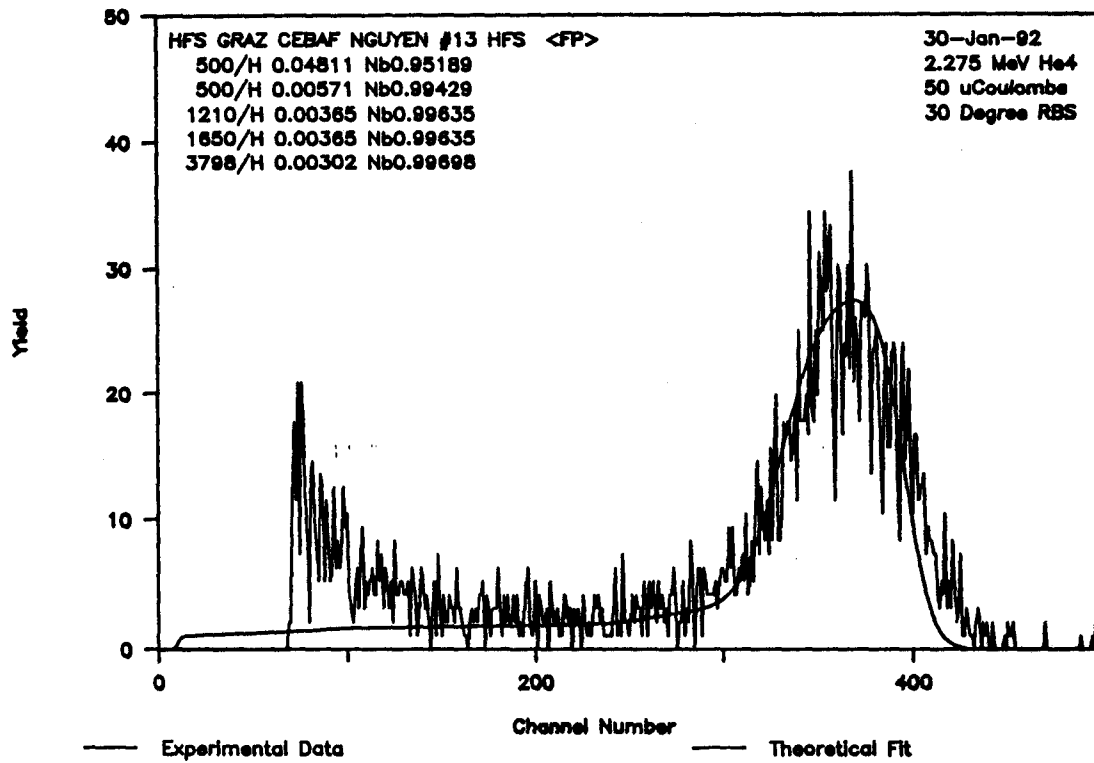


Figure 3. High RRR - as received

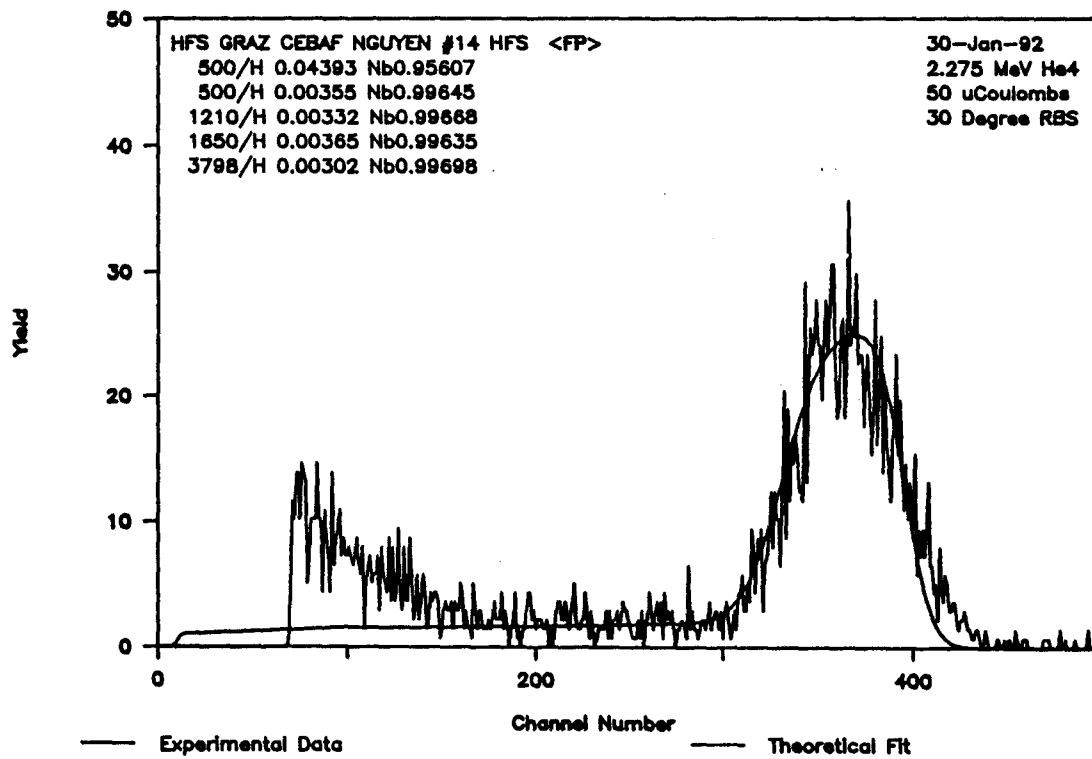


Figure 4. High RRR - BCP (90 μ m)

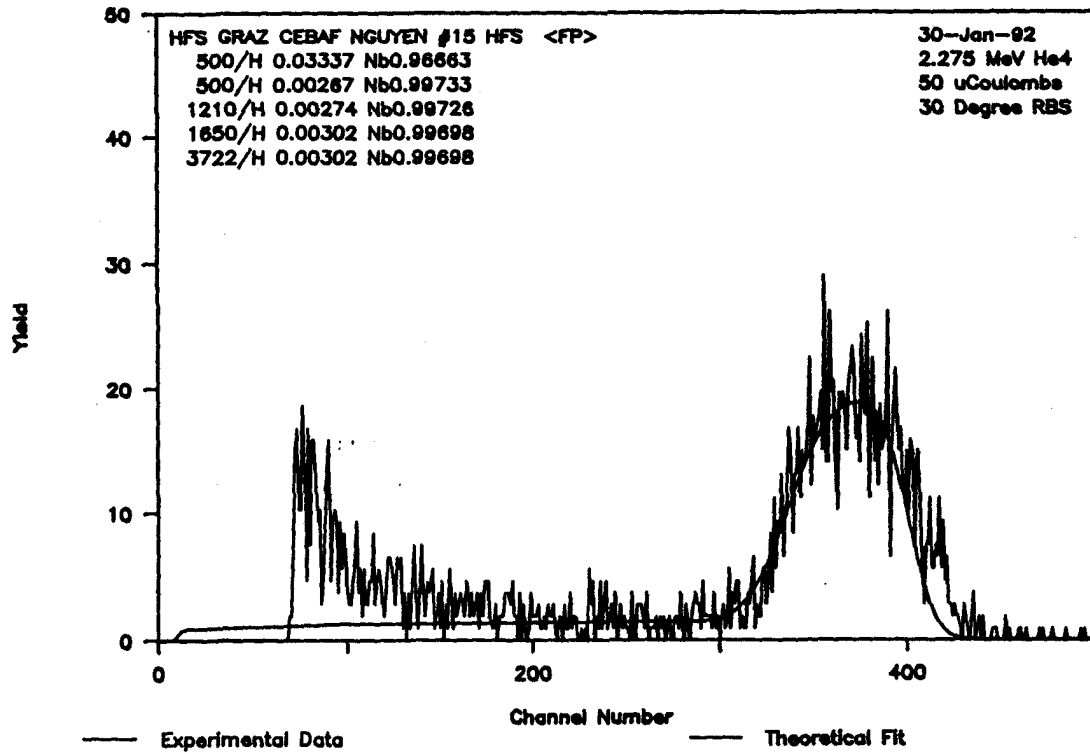


Figure 5. High RRR - BCP (90 μ m) - HT 800 $^{\circ}$ C

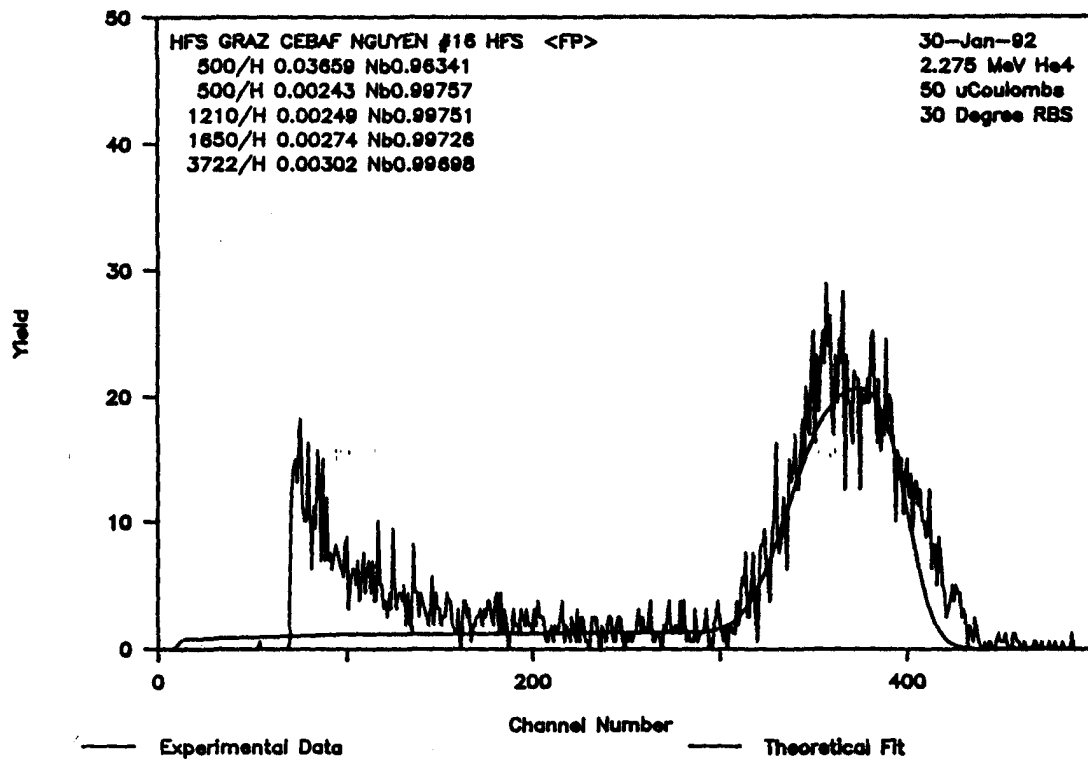


Figure 6. High RRR - BCP (90 μ m) - HT 800 $^{\circ}$ C/Ti

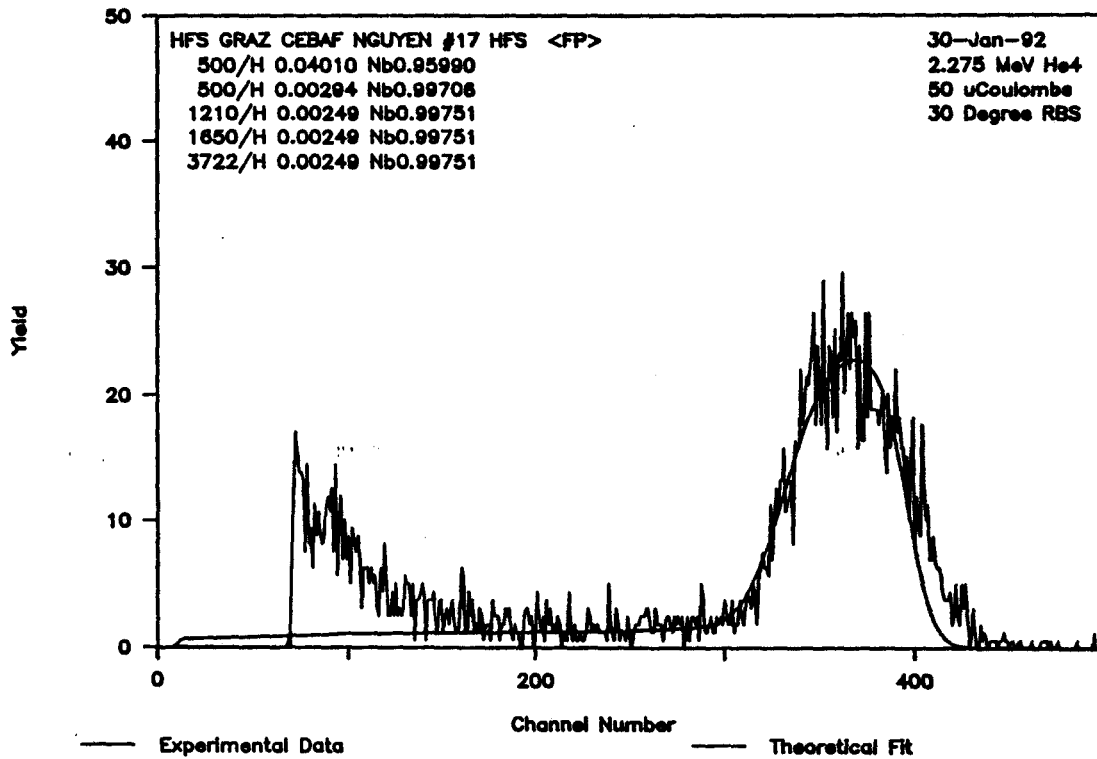


Figure 7. High RRR - BCP (90 μ m) - HT 800°C/Ti - BCP (1mm)

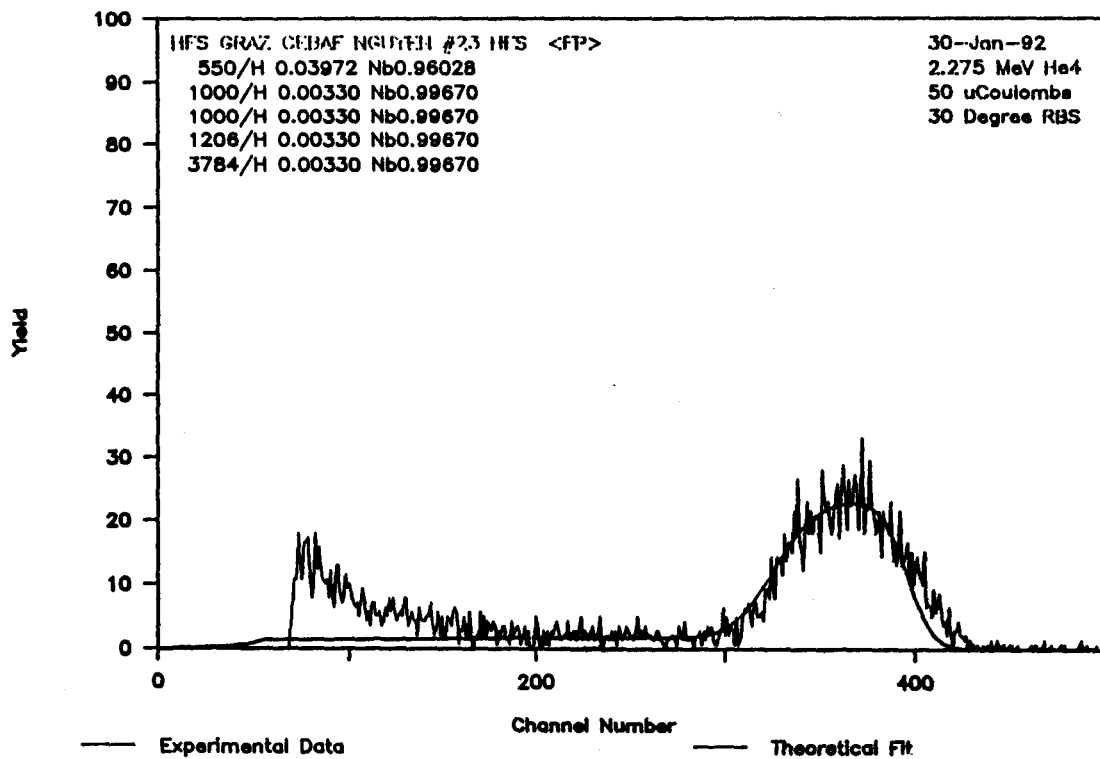


Figure 8. High RRR - CP at 23°C (90 μ m)

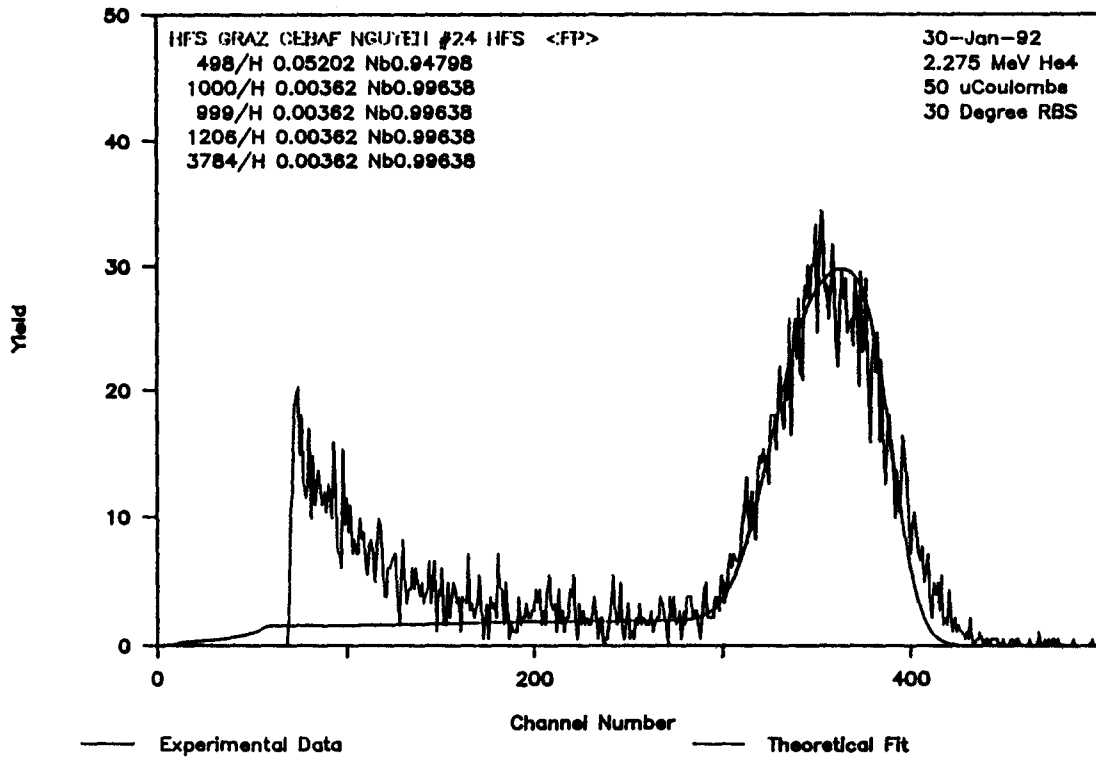


Figure 9. High RRR - CP at 28°C (95 μm)

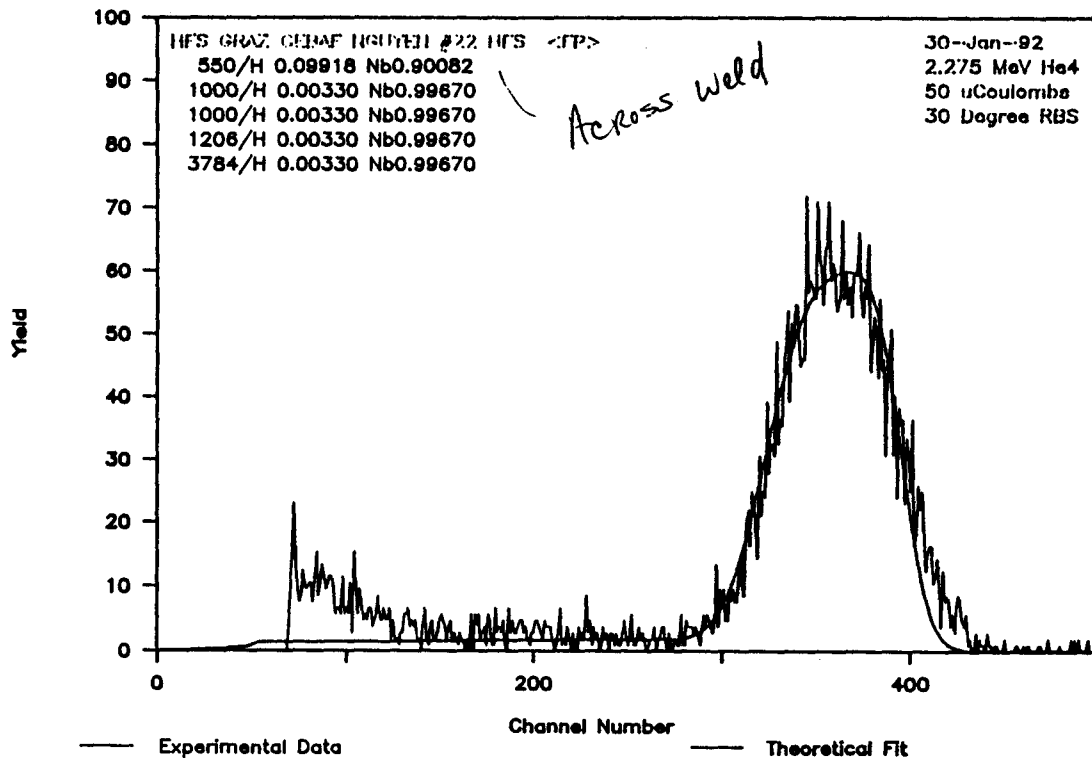


Figure 10. High RRR - EBW

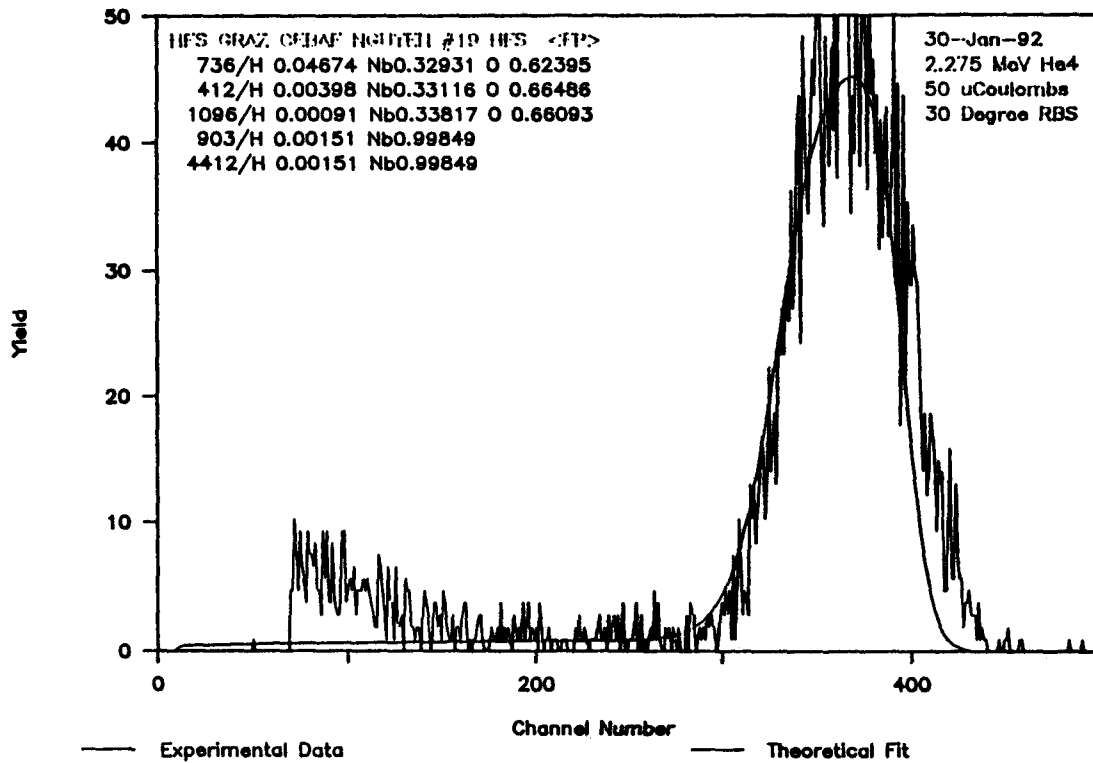


Figure 11. High RRR - BCP (90 μ m) - anodized 100V

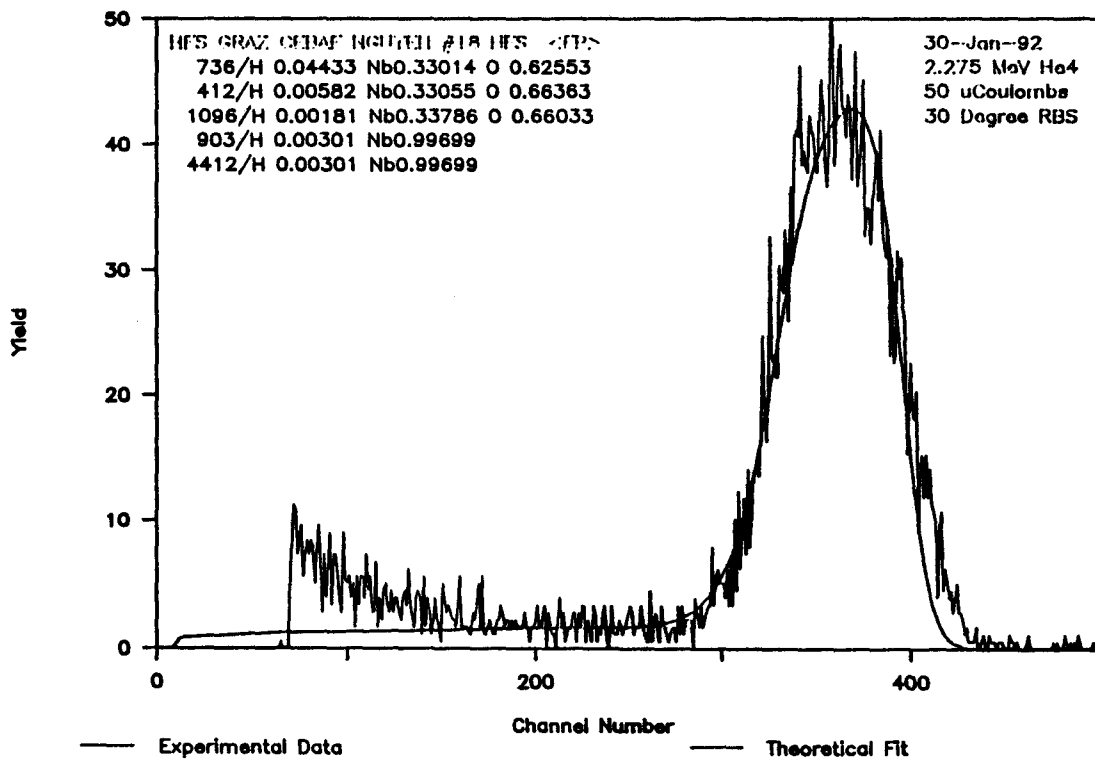


Figure 12. High RRR - BCP (90 μ m) - anodized 100V - 260 $^{\circ}$ C/5hours

Figure 13

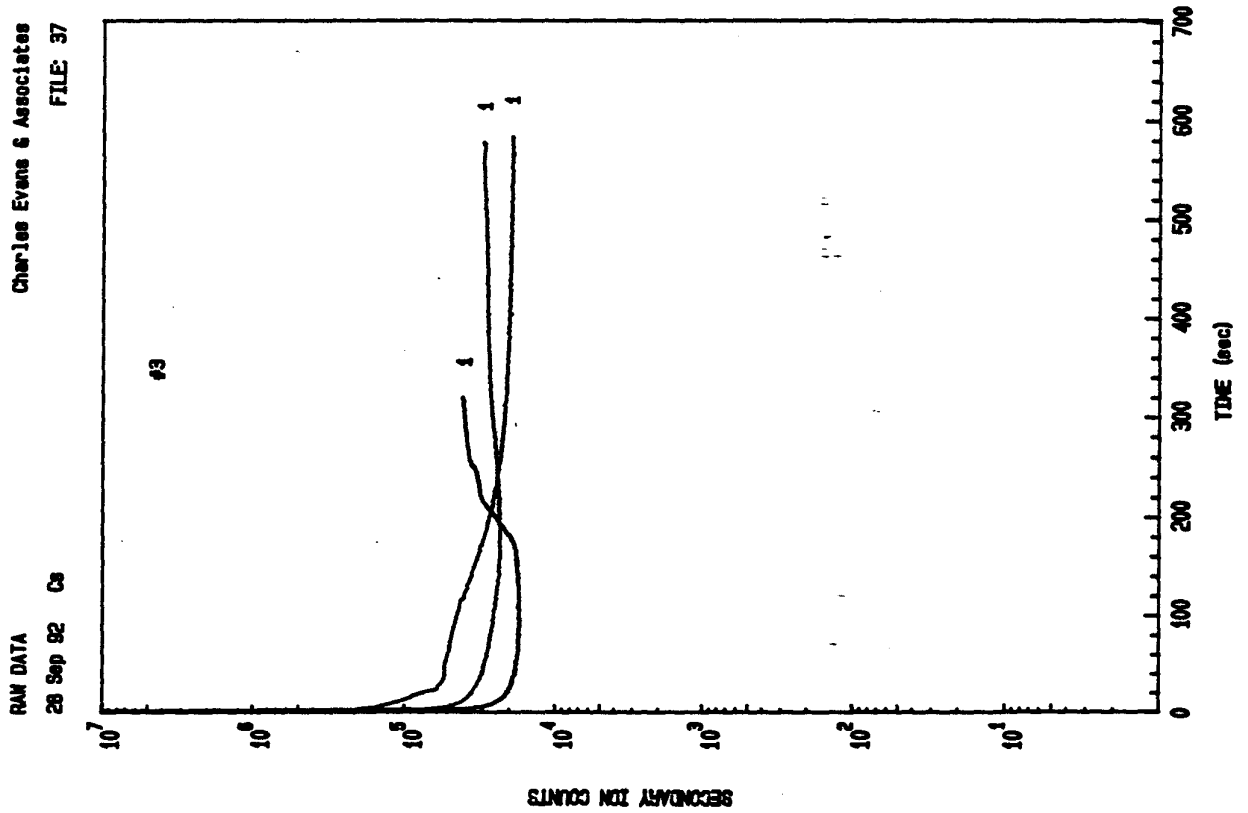
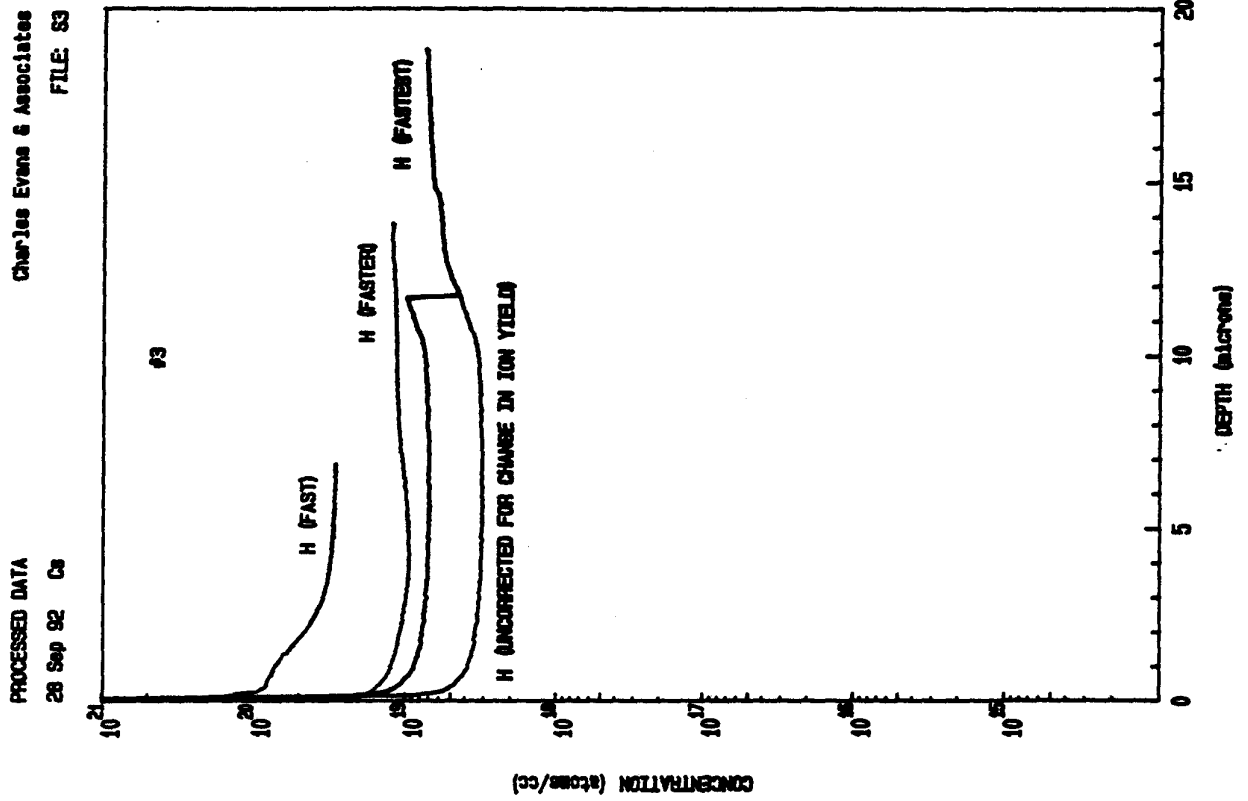


Figure 14

