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Minutes of the Tank Waste Science Panel Meeting February 7-8, 1991

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Summary

The Tank Waste Science Panel met February 7-8, 1991, to 1) review the latest data from the analyses of the October 24, 1990, gas release from Tank 241-SY-101 (101-SY) at Hanford, 2) discuss the results of work being performed in support of the Hanford Tank Safety Project, and 3) be briefed on the ferrocyanide issues included in the expanded scope of the Science Panel.

The shapes of the gas release curves from the past three events are similar and correlate well with changes in waste level, but the correlation between the released volume of gas and the waste height is not as good. An analysis of the kinetics of gas generation from waste height measurements in Tank 101-SY suggests that the reaction giving rise to the gases in the tank is independent of the gas pressure and independent of the physical processes that give rise to the episodic release of the gases. Tank waste height data were also used to suggest that a floating crust formed early in the history of the tank and that the current crust is being made thicker in the eastern sector of the tank by repeated upheaval of waste slurry onto the surface.

The correlation between the N_2O and N_2 generated in the October release appears to be 1:1, suggesting a single mechanistic pathway. Analysis of other gas generation ratios, however, suggests that H_2 and N_2O are evolved together, whereas N_2 is from the air. If similar ratios are observed in planned radiolysis experiments at Argonne National Laboratory, radiolysis would appear to be generating most of the gases in Tank 101-SY.

Data from analysis of synthetic waste crust using a dynamic x-ray diffractometer suggest that, in air, organics are being oxidized and liberating CO_2 and NO_x. Experiments at Savannah River Laboratory indicate that irradiation of solutions containing NO_3^- and organics can produce N_2O.

The Science Panel has been asked to examine the chemistry and physics of waste in tanks containing ferrocyanide. Members were briefed on the ferrocyanide process used in the 1950s to remove the ^{137}Cs from the Bismuth Phosphate wastes at Hanford and what is known about the chemistry of the process.

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Minutes of the Tank Waste Science Panel Meeting
February 7 & 8, 1991

Introduction

The fourth meeting of the Tank Waste Science Panel (Science Panel) was held on February 7 and 8, 1991, at the Registry Hotel in Denver, Colorado. The agenda for the meeting is provided in Attachment A. The list of those attending is given in Attachment B.

During this meeting the latest data obtained from the analyses of the crust samples, the gas analyses, and other physical measurements taken during the October 24, 1990, gas release event from Tank 241-SY-101 (Tank 101-SY), and the latest data obtained by the Science Panel members and the research programs funded through Westinghouse Hanford Company were presented and discussed. Also during this meeting, the role of the Science Panel was extended to cover the ferrocyanide-containing tanks at Hanford. To introduce the Science Panel members to this subject, several presentations were made.

All topics in the agenda were all discussed but not in the order in which they appear in Attachment A. In addition, two speakers were added to the agenda.

Day One of the Meeting

The first day of the meeting consisted primarily of presentations on the latest gas release event and work performed at Pacific Northwest Laboratory[a], Washington State University, Westinghouse Idaho Nuclear Co., Georgia Tech, Savannah River Laboratory, and Argonne National Laboratory. These presentations were preceded by discussions on the expanded scope of the Science Panel, the charters of other related task forces and panels, funding procedures, and coordination of research efforts.

General Panel Business

The final version of *Chemical and Physical Processes in Tank 241-SY-101: A Preliminary Report* (Tank Waste Science Panel 1991), less the final cover, was distributed to those in attendance. The final cover will have an artist's sketch of the SY Tank Farm on it.

Thom (T. H.) Dunning indicated that on Friday the scope of the Science Panel would be expanded to include the ferrocyanide wastes. He requested that the Science Panel members suggest names of persons having some expertise pertinent to the ferrocyanide issues who might serve on the Science Panel. Thom also suggested that a small group of people be assigned the task of writing a document that discusses the literature relevant to the ferrocyanide issues and identifies the critical issues. The Science Panel members thought this would be a good idea, especially in light of the success of the last survey report (Strachan, Reynolds, Siemer, and Wallace 1991).

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One of the Science Panel members asked L. G. (Larry) Morgan to summarize the charters of the other task forces and panels that have been assembled to study the Tank 241-SY-101 and ferrocyanide issues. Larry said that he would be willing to write a letter to the Science Panel members explaining the charters of the various panels and the role that the Tank Waste Science Panel plays in the overall effort to understand the issues and the waste problems currently faced by DOE. In summary, Larry said that there are four committees/panels: 1) the Defense Nuclear Facilities Safety Board (DNFSB), which was mandated by Congress, 2) the Advisory Committee on Nuclear Facility Safety ("Ahern Committee"), which was chartered by Secretary Watkins, 3) the High Level Waste Tank Task Force, which was chartered by Mr. Leo Duffy, and 4) the High Level Waste Technical Advisory Panel, which reports to the High Level Waste Tank Task Force. The Tank Waste Science Panel was proposed by members of the PNL staff and recommended by Mr. Duffy to be funded through Westinghouse Hanford Company. The work of the Science Panel has been noted by the other task forces/panels.

The Science Panel members then entered into a serious discussion about how the research recommended by the Science Panel is being funded by Westinghouse Hanford Co. The contract for the work at Argonne National Laboratory had recently been funded, but not without some lengthy discussions about cost and schedule. The work at Georgia Institute of Technology had not yet been funded. It was noted that no steps had been taken to initiate the recommended experimental work on the physical phenomena taking place in the tank. There was substantial concern about the negotiation of the contracts. The language in the contract was more appropriate for the purchase of a number of widgets than for the funding of research. One clause that was particularly troublesome indicated that if the staff at Westinghouse was unhappy with the results of the research, they reserved the right to request their money back. In part, the problems seemed to stem from the use of a contract that is inappropriate for funding research and from the use of a government contract in which research is placed in a restrictive package. Some changes appear to be needed in order to facilitate contracts for research on issues as important as the issues associated with Tank 241-SY-101.

Another area of concern is that the research at the three institutions has become too narrowly focussed. The Science Panel recommended a program with some overlap in the studies. This is needed to provide a measure of quality assurance in research involving either new techniques or new applications of old techniques. Each scientist approaches a problem from a slightly-to-dramatically different perspective. Under normal circumstances, a result obtained by one researcher is checked by the work of another in the normal course of scientific endeavor. Because of the seriousness of the issues associated with Tank 101-SY and the limited time over which the research is to be performed, the program funded through Westinghouse Hanford Company must contain this duplication in order for the results to have maximum credibility. This is not currently being done.

Kinetics of Gas Generation and Crust Formation

In analyzing the kinetics of gas generation in Tank 101-SY, D. M. (Denis) Strachan decided to determine whether useful information was hidden in the waste height measurements that have been recorded since the first waste was placed in the tank in 1978. A brief description of his analysis of the kinetics of gas generation as determined from the waste height measurements is provided in Attachment C. In his presentation, Denis showed how the waste height measurements indicated that the gas generation rate was constant with time between individual gas release events. This suggests that the reaction giving rise to the gases in the tank is independent of the gas pressure and independent of the physical process that gives rise

to the episodic release of the gases. In other words, the physics of the system give rise to the collection and episodic release of gases that are being generated through a chemical mechanism that appears to be at steady state.

In addition, Denis suggested that, over the temperature range observed for the waste near the bottom of the tank, the rate appears to be independent of temperature, although the temperature variations are small and the height measurements imprecise. Assuming an activation energy for a first order reaction that is equal to the activation energy determined by Delegard (1981) or D. D. (Duane) Siemer (see Attachment F), one would expect to see curvature in the tank height data between gas release events. Instead, he observes that the data are linear with time and that the standard deviation in the slope of most of the lines through the data is less than 3%.

Denis then plotted the slopes of the lines determined from one gas release event per year since 1984 against the time since the gas release events were first observed (1984 = 0 days). At first the data appeared to be too scattered to draw many conclusions. However, he suggested that the rate of gas generation may have increased during the period of air lancing. The data are also consistent with a decreasing rate in the long term that is linked to the decay of either ^{137}Cs or ^{90}Sr. While both of these observations need to be investigated further, they are important clues to the mechanisms by which the gases are generated in Tank 101-SY. For instance, these observations are consistent with two mechanisms - one driven by radiolysis and the other by the chemical mechanisms. In one case the primary radiolysis reactions are rate limiting and in the other a key rate limiting species in the radiolytic process is generated by a chemical reaction.

After attending several meetings in which crust-related subjects were discussed and after looking over the waste height measurements as obtained with the Food Instrument Corporation (FIC) gauge and the manual tape, Denis noted a trend in the data that was suggestive of the mechanism by which the crust is formed. He noted that the gauges read nearly the same as when they were removed in November 1990 and replaced with newly calibrated instruments. This indicated that the data collected earlier were reliable. He plotted the difference between the height as measured using the FIC gauge and the height measured using the manual tape. The very early data (first four data points in Figure 12, Attachment C) suggest that a crust formed very soon after the first waste was added to the tank in 1978. Three more additions were made over the next 12 months and yet the manual tape measurements yielded higher waste heights than did the FIC (a negative difference between the FIC and the manual tape). The difference remained negative until shortly after the last addition of waste to the tank in 1980. Soon after the last addition, the episodic release began and the difference between the FIC and manual tape readings began to increase. Because the manual tape readings after 1984 have not yet been made available to Denis, he has been unable to continue the analysis to the present day. However, the current difference between the FIC and the manual tape is about +20 inches.

This information, along with the gamma scans and the pictures of the waste surface in the tank, is consistent with a model in which part of the crust forms by ejection of liquid waste from below the crust onto the top of the crust predominantly in the eastern to northeastern sectors of the tank. This would account for the observed high gamma activity in the crust area (see Attachment E) and for the high FIC gauge readings relative to the manual tape readings. Additional data will be analyzed when they are received.

Numerical Simulation of the Thermal Profile in Tank 101-SY

At PNL, numerical simulations have been carried out by R. T. (Rudy) Allemann and co-workers out using the TEMPEST code. The material was presented by D. S. (Don) Trent and included color vu-graphs and a video, neither of which are reported here. Several assumptions were used in generating these simulations because the correct algorithms have not been included in the TEMPEST code nor are these changes being funded. The heat load in the tank was assumed to occur near the bottom of the tank. A fixed particle size distribution was assumed and these particles were assumed to settle at a constant velocity. Don said that a settling velocity of 0.1 ft/s was too high to explain the changes in the thermal profile that were observed in Tank 101-SY on October 24, 1990. Good results were achieved with a settling velocity of 0.01 ft/s. These calculations, therefore, give an order of magnitude estimation of this important physical parameter.

The calculations carried out by Rudy and his co-workers indicate that they can simulate the thermal profile of the tank reasonably well. Their calculations suggest that the waste movement during a burp occurs predominantly along the walls of the tank, but not all of the waste from the lower portion of the tank flows up the walls. Some of the waste breaks loose from the rest of the hot waste and can flow upward from the point of the first instability. The time over which the waste turns over is very short - on the order of 30 to 50. This time is consistent with the observed times for the October 24 gas release event.

Analysis of Synthetic Crust Using Dynamic X-Ray Diffraction

A portion of synthetic waste crust generated by D. L. (Dan) Herting (WHC) was taken to W. J. (Bill) Thompson at Washington State University for analysis using a dynamic x-ray diffractometer. Bill reported on the use of this instrument and on the results from this sample of synthetic waste crust.

A dynamic x-ray diffractometer can be used to obtain information on the crystalline phases present in a sample as the sample is heated at a given heating rate. Since this instrument is operated in a similar fashion to a differential scanning calorimeter (DSC) or thermogravimetric analysis (TGA) instrument, the results from the dynamic x-ray diffractometer can be used to determine what phases are present in a sample and correlate phase changes with the information on mass loss and heat input or output. In addition, the instrument can be operated with air or with an inert gas in contact with the sample, and the gas phase can be analyzed to determine which, if any, gases are being evolved as the sample is heated.

Bill showed results that indicated $NaNO_3$, $NaNO_2$, Na_2CO_3, and $Na_2CO_3 \cdot H_2O$ (the latter identification was tentative) are present at 90°C in the synthetic crust (see Attachment D). At about 200°C, melting appears to occur. In a N_2 atmosphere, the decomposition of the crust generates CO_2 at 200°C and NO_x at about 300°C. The NO_x is measured using a chemiluminescence detector that is not sensitive to N_2O. In air, there is evolution of CO_2 at both 200°C and at 300°C with the second peak being much larger than the first. The evolution of NO_x in air occurs at about 400°C and is larger than the peak observed in N_2. In the DSC, there is an exothermic peak at about 200°C. The data suggest that in air the organics are being oxidized and liberating CO_2 and NO_x. More data are needed, however, especially the DSC measurements of the synthetic crust in air.

Data from the October 24, 1990, Gas Release Event

Results from the October 24, 1990, gas release event were divided into two parts, one presented by D. L. (Dan) Herting (WHC, invited) and the other by D. A. (Dan) Reynolds (WHC). Dan Herting presented the results obtained from the samples that were recovered from the surface of the crust by removing three instruments. The results from his own gas generation experiments with surrogate wastes were presented. Dan Reynolds reported on the data taken during the October 24th event.

Dan Herting presented the same material that he had presented to the High Level Waste Tank Task Force in January 1991. He emphasized that the main goal of these analyses was to determine if it would be safe to take a sample of the crust after the next gas release event. The results from these analyses are shown in Attachment E. The samples were obtained by removing the manual tape, the FIC gauge, and a sludge weight. A sludge weight is essentially a steel ring with a heavy bail to which a cable is attached for raising and lowering the weight. The sludge weight contained three types of material, classified as "SW/Dry," "SW/Wet," and "SW/Loose." The "SW/Dry" material came from the outside of the weight and the "SW/Wet" from the inside. The sample labeled "SW/Loose" came from inside of the retrieval device for the sludge weight and probably spalled from the cable during retrieval. The manual tape contained very little material. The FIC plummet contained more, but much less than the sludge weight. The analyses of these materials are shown in Attachment D, Tables 1 to 4 (E.9 to E.13).

Dan showed that the recent samples of the crust were similar to the samples reported by Mauss in 1986 (Mauss 1986). More importantly, however, was the similarity among all of the retrieved samples and the similarity among the samples and the synthetic crust. The latter point is important because of the confidence it gives to the studies that will be performed with synthetic crust materials.

Dan also reported on some of the experiments he has running in the laboratory. Some of the data were obtained recently and he had not had time to fully analyze them. Dan has been collecting gas generation data in an all-glass apparatus. The pressure data are shown in Figure E.15 and are obtained by periodically removing gas to the evacuated gas sampling bulb. Sampling of the gas phase causes the gas pressure to decrease, but when the data were corrected for the periodic pressure change no effect is evident. It was pointed out that this would be consistent with Denis Strachan's discussion earlier and would suggest that the reaction is zero order in the gas pressures. Dan observed that the gas generation was delayed by about 4 days at 100°C during which no detectable gas was released (no pressure increase). Analyzing the pressure data, Dan fitted his data to the first order expression in the pressure, the measured physical parameter:

$$P = P_0 + (P_s - P_0)\exp(-kt) \qquad (1)$$

where P is the pressure, k is the rate constant, and t is the time. The least squares fit of the data yielded values for P_s, P_0, and k of 939 torr, 302 torr, and 0.0031 min^{-1}, respectively.

The results obtained by Dan are all consistent with the earlier work by Delegard (1980). Dan observed that the ratios of the gases were different from the ratios observed in the gases emitted from the

tank. Nitrogen gas was observed as a reaction product and O_2 was observed to be consumed in the reaction. Dan has used several organics in his experiments, but he has found that HEDTA reacts the fastest.

Dan Reynolds started his presentation with the results taken during a series of gamma scans of Tank 101-SY. Normally, these scans are taken in a liquid observation well (a closed-end tube inserted permanently in the tank and extending from the top of the tank to the bottom) in single-shell tanks to determine the height of the liquid and the waste. Gamma scans are obtained by lowering the gamma detector into the liquid observation well and recording the gamma flux coming from the waste. A typical scan is shown in Figure F.3. In double-shell tanks, however, there are no liquid observation wells. To obtain a gamma scan for Tank 101-SY, the gamma detector was lowered through risers positioned in the annulus between the inner and outer tanks. The risers used for these observation are shown in Figure F.4 and the resulting gamma scans in Figure F.5 (the rise positions are the same in both figures; the numbers are different because there are two related numbering schemes for the risers). Only the scans taken through riser 9A (78) are significantly different from the other scans. It is uncertain why this one is different, but it could be related to the proposed crust formation mechanism.

It was anticipated that differences could be detected as a function of time and would lead to a better understanding of the processes taking place in the tank. However, the scans have not changed dramatically over the interval between October 30, 1990, and the last scans, which were taken in January 1991. The constancy of these scans is shown in Figures F.6 and F.7 (Figure F.7 is a superposition of the December 13, 1990, scan on the October 30, 1990, scan). To show that other changes were occurring over the same time period, the temperatures are shown superimposed on the gamma scans in Figure F.8. There is no correlation with the ^{137}Cs content of the tank as shown in Figure F.9 in which the ^{137}Cs concentrations of the "bottle on a string" samples is shown. [In a separate meeting after the Science Panel meeting, Dan Herting indicated to the author that there appears to be a dilution error in the data reported by B. Mauss. Therefore, the ^{137}Cs concentration for the top sample should be closer to the ^{137}Cs concentrations of the other samples as should the concentrations of the other constituents and the density.] As yet there is no definitive explanation of the gamma scans, but one proposed explanation is that material is coating the tank walls. The gamma detector has a depth of view of about 20 cm. Anything crystallized on the tank walls would play an important role in how much gamma radiation reached the detector. There is some evidence that this material could contain substantial ^{137}Cs and hence give rise to higher gamma radiation in certain regions.

Dan Reynolds then summarized the results from the October 24th event in more detail than had been sent to the Science Panel members earlier. Most of the pertinent data are shown in Figure F.10 and F.11. Raw data from the strip charts are shown in Figure F.12 albeit in a somewhat confusing manner because of the lack of color to differentiate between the curves. Each of the curves has been labeled; the numbers on the second line from the bottom are for the pressure scale (-4" to +1" of water gauge). The pressure readings went off scale, but a separate recorder is used for the high range. Thus, pressure data were not lost. The flow rate measurements also go off scale and for these there was no expanded scale. The other curve shows the volume percent H_2. Good agreement between the three methods of measuring H_2 is shown in Figure F.13. This gives good assurance that the thermal conductivity instrument has been giving accurate and reliable results.

Computer simulations of the gas release events have been performed using the FATHOMS code. This code can be used to calculate the evolution of the gases from the tank and the mixing of those gases

in the tank plenum. Assumptions have to be made about the composition of the gas entering the tank plenum and the assumption has been made that the gas is 30% N_2O, 30% H_2, and the remainder N_2. This assumption has led to reasonable agreement between the calculated and the observed releases (Figure F.14). The third column in this figure has gas volumes that are too low; the hand written numbers are better estimates of the gas volumes.

A comparison of the past three gas release events is shown in Figures F.15 and F.16. The shapes of the releases are similar and correlate with the changes in the waste level, but the correlation between the released volume of gas and the waste height is not as good.

Dan also addressed the issue of inerting the tanks using N_2 or some other gas. In the past, adding inert gas to the tank has always been considered to be economically and logistically difficult because of the large volumes needed. Dan showed that by injecting the inert gas in the region in which the gases are being generated, one could use much more manageable volumes of gas to decrease the H_2 concentration to levels below the flammability range. To do this Dan constructed a ternary diagram on which is plotted the N_2, H_2, and N_2O concentrations. Dan's best estimate of the gas composition is shown as a filled circle the other circles represent gas mixtures based on the analysis of data from the tank. The lower flammability limits are drawn on the diagram. To dilute the reactive mixture with air would require about five times more gas than if N_2 was injected to the area where the gases are being generated. The show stopper here, however, is the feasibility of adding the N_2 in the areas where it is needed and getting the distribution that is needed.

Hydrogen Production From Organics and the Measurement of Trace Quantities of Hydrogen

One of the key measurements that could shed light on the mechanism of gas release in Tank 101-SY is the measurement of trace quantities of H_2. A method was developed and reported earlier (Strachan and Morgan 1991) by D. D. (Duane) Siemer (WINCO). During the development of this method, Duane discovered that some organics react to produce H_2 from strongly alkaline aqueous solutions. The apparatus that Duane developed is shown in Figure G.2 (see Attachment G). There are two key parts to this apparatus - a trap for unwanted volatiles and a combustor to convert H_2 to H_2O. Gases from the test are routed through the traps where all interfering gaseous species are removed. Interfering gaseous species include H_2O, formaldehyde, and other volatile organics. The cleaned gas stream contains the base gas (air, argon, or other atmosphere under which the experiment is being performed) plus the H_2. The H_2 is then converted to H_2O and it is this H_2O that is detected using a sensitive moisture detector. A sample output from the detector is shown in Figure G.3. Duane has been very careful to check for all the possible interferences and the specificity of the catalyst used in the combustor. The apparatus is very sensitive toward the detection of H_2 as shown in Figure G.5.

Duane then went on to discuss his experiments on the generation of H_2 from organics in highly alkaline solutions. The test apparatus for doing these experiments is shown in Figure G.6. The apparatus is very simple but displays some very ingenious thinking. These apparatuses are not connected to the H_2 detector all of the time but are allowed to run independently. A bead of condensate forms in the lower part of the condenser and forms a seal, thus preventing the loss of H_2. Hydrogen is determined on a periodic basis by connecting the top of the condenser to the detector. However, both batch and continuous methods can be used. A sample output from a continuous detection of H_2 is shown in Figure G.8.

Duane showed that there may be a high solubility of H_2 in these highly saline solutions (Figure G.9). It has always been assumed that H_2 has only a very limited solubility in these solutions - a solubility about the same as for H_2O. This appears to be an incorrect assumption and may need to be further investigated.

Duane's conclusions from his research are shown in Figure G.10 and G.23. The intervening figures support these conclusions and are only briefly described here. One of Duane's observations from earlier work is that the organics originally in the waste are probably no longer there. He bases this argument on the work by Strachan et al. (1986) in which it was concluded that after about 80 hours organics in a synthetic Tank 107-AN waste mix had been degraded to other organics such as iminodiacetic acid (IDA). [Note: In most of the figures the "y" axis is labeled "μa Response." This refers to the amount of H_2 generated in the test (see Figure G.5).] From his work, Duane concludes that one can account for about half of the H_2 production in Tank 101-SY by chemical means.

In the discussion that followed, it was mentioned that the other experimenters note a delay time of about 4 days. This delay time was mentioned by Dan Herting, E. C. (Gene) Ashby, and Dan Meisel. In their experiments, however, they are trying to measure gas production by increases in the pressure in their apparati or by displaced liquid volume. It is uncertain why Duane sees H_2 production immediately. However, in his experiments he uses a flowing gas stream that is bubbled through the solution. [It is possible that there is a link between Duane's observation of a relatively high solubility of H_2 in these solutions and the delay observed by other experimenters who do not purge their systems. It should be noted here also that this is one of the main reasons why there is a need for healthy overlap between the work being performed at the various institutions. Each experimenter, while ostensibly performing the same experiment, brings a slightly different approach to the problem.]

Chemical Mechanisms Studies at Georgia Institute of Technology

A very competent team has been assembled at Georgia Tech. These scientists include E. C. (Gene) Ashby (Organic Chemistry), Kent Barefield (Inorganic Solution Chemistry), Charles Liotta (Organic Kinetics), and Henry Neumann (Nuclear Chemistry and Kinetics) (Figure H.1). In the absence of a contract, these people have been meeting regularly to discuss the problem, the experimental approach, and the theory underlying the chemistry. They have been doing some work on their own because of the perceived importance of this problem. The following is a summary of their work to date.

Gene and his coworkers determined that part of the reason for some discrepancies may be due to the lack of an agreed upon standard solution with which all those working on the project can compare results. The team at Georgia Tech suggests that we agree to use an initial solution that is free from solids; this would eliminate some of the confounding issues that occur in the presence of solids. Gene has been an advocate of performing very specific and careful experiments, some of which are shown in Figure H.4.

Over the intervening months since the last meeting, Gene has been in contact with Duane and they have been sharing results. According to Duane's results, the dominant reaction product should be oxalate, given that glycolate is the primary reactant. Glycolic acid was used in B-Plant as noted in one of the previous meetings. Glycolate-like fragments may also come from the decomposition of other organics in the original mixture. Based on Duane's results, Gene suggests that a study with formaldehyde and D_2O be carried out to resolve the reaction mechanism. The reaction mechanism can be further verified using mixed aldehyde reactions such as those proposed on page H.6.

As part of the Georgia Tech team, Dr. Charles Liotta has been studying the kinetics of gas evolution from simulated waste solutions. The apparatus he has been using is shown in Figure H.8. In this apparatus, gas volumes as low as 0.1 cm^3 can be measured. A gas sampling bulb is used to collect samples for gas analyses, but no gas analyses had yet been performed because the funding had not yet been authorized. As noted above, there is a need to have a standard homogeneous solution for kinetics work. The composition of the proposed standard solution is shown in the table on H.9. Some solids may form in this solution as the reaction proceeds if CO_2 is one of the reaction products. While this particular composition may not be adopted, there is a need for a standard solution that can be used as a point of reference for the testing. Initial results from the use of the apparatus are tabulated on page H.10 and graphed on page H.11. These data indicate a delay in the start of the reaction of about 4 days. This delay in the start of the reaction is not observed by Duane in his experiments. Other experimenters have observed the same delay period in their experiments. These data have not been corrected for temperature and pressure.

There was some discussion about the delay time in the production of gases observed by some. Since the conditions under which all of these tests have been performed are similar, some Science Panel members felt that the delay time is an artifact of the apparatus used in the experiments. Higher than expected gas solubilities, for example, could explain the observed differences between Duane's results and the results from other experimenters.

One of the tools used by organic chemists to identify organic species is nuclear magnetic resonance (NMR). This technique is being used by Dr. Kent Barefield of the Georgia Tech team to determine the rate at which reaction products are formed in the standard solution, the nature of these products, and the hydrogen exchange for the HEDTA species. Isotope labeling has been suggested as a method of determining the source of hydrogen in these solutions. If, however, the hydrogens on the organic molecule freely exchange with hydrogen in aqueous solution, then labeling these positions on the organic molecule will lead to false results. To this end, HEDTA was placed in a solution of D_2O to see how fast the H and the D exchanged. Kent also looked at the feasibility of using ^{13}C NMR as a technique for examining the decomposition products of HEDTA and other organic species. The objectives and initial conclusions of his assessment are shown on page H.13.

The NMR spectra of HEDTA after being in the standard solution for 48 h and 168 h are shown on page H.14. A stick model of the molecule is shown in which the chemically different hydrogen positions are shown. The peaks in the spectra that result from the hydrogens at these positions are also illustrated. For comparison, the HEDTA spectrum before reaction is shown on page H.15. Note in the HEDTA spectrum that the central peaks are split due to replacement of the H atoms by D atoms. The intensities of the peaks changes dramatically when HEDTA is in contact with the standard solution for only 48 h. Likewise, the ^{13}C NMR spectrum shows significant changes between 48 h and 168 h.

Over the past months since the last meeting, the team at Georgia Tech has been analyzing the data from two reports (Delegard 1980 and Strachan and Morgan 1991 [see Attachment H]) and the calculation by Dr. Steven Agnew (Los Alamos National Laboratory) of the energy potentially produced by the decomposition of EDTA. Dr. Henry Neumann has been examining these reports and calculations and the results of his examination are reported in Attachment H. After reviewing the report written by Delegard (1980), Henry concluded that it may be difficult to reproduce Delegard's work because the method and exact composition of the solution he used are not given in the document. From his analysis of the data and the uncertainties he identified, Henry suggests, as noted above, the use of a homogeneous solution for the systematic investigation of the reaction kinetics.

In response to the radiolysis reactions proposed by E. J. (Ed) Hart that had been distributed to the Science Panel members, Henry suggested that the principal oxidizing agent should be NO_3^- which would result in a suite of reduced nitrogen-bearing species. Although NO_2 should form as a result of the reduction of NO_3^-, it would be expected to be present for only a short period of time because the reaction rates are very fast. Henry used the values of the reaction kinetics reported by Ed. [If these reaction schemes are correct, there should be a significant change in the NO_3^- and NO_2^- concentration when new samples are taken from Tank 101-SY and when these values are compared with those obtained in 1986.]

In a presentation to the Hanford Nuclear Waste Tank Task Force, Steven Agnew proposed a reaction that provides, at least in part, the energy to sustain the temperatures in the tank. In this reaction (H.22) Steve shows N_2O, N_2, CO_2, and H_2 as the gaseous reaction products. However, Henry suggests that the reaction product from oxidation by NO_3^- would be expected to be predominantly NO_2^-. The products N_2O and N_2 would be expected to result from the reaction of the amine nitrogens with NO_3^- or NO_2^-. Other reaction schemes could be written that would be more in line with the suggested chemistry than the one Steve used. These reactions are shown on page H.23. All of these net reactions yield as much energy as the one suggested by Steve, however the rate at which this energy is released depends strongly on the complexity of the reaction mechanism and on the rate at which the overall reaction is completed. Henry's conclusions are shown on page H.24.

Some consideration was given to why the crust floats. The density of the crystals should be greater than the density of the liquid underlying it. One possibility suggested by Henry is that a solid solution of $NaNO_3$ and Na_2CO_3 supports the crust. The charge neutrality could be accommodated by vacancies. [The phase diagram for the $NaNO_3$-Na_2CO_3 system shows no solid solution at either end of the composition range.]

Gene and his coworkers also examined the gas analyses from the October 24, 1990, gas release event. From their analysis, the data suggest a strong correlation between the N_2O and N_2 data. The analysis suggests that there is a 1:1 correlation between the two gases. That this is a coincidence is unlikely and suggests, or rather limits, possible reaction mechanistic schemes.

Radiolysis Work at Savannah River Laboratory

At Savannah River, experiments with solutions containing NO_3^- and NO_2^- have been carried out for a number of years in an effort to determine the role of these ions in the radiolysis chemistry of the wastes stored at Savannah River Plant. The results of these studies were presented by Dr. N. E. (Ned) Bibler.

In one experiment, a long tube was inserted into one of the waste tanks such that the end was well beneath the liquid waste. The inside of the tube was evacuated until the waste was drawn to the maximum height. A valve at the end of the tube outside of the tank was then closed. With time, the waste height decreased as gases were evolved from the waste. After some time, the gases were sampled for analysis. The gas composition was found to be 36.8% N_2, 56.4% O_2, and 7.5% H_2. After correction for the amount of air in the sample, the gas had a O_2/H_2 ratio of 6.1 (86%/14%), which is typical of the gas composition above a strongly alkaline solution that is 3 M to 4 M NO_3^-. The correction for air was made assuming that N_2 was not a radiolysis product, which is reasonable for the waste solutions at SRS. The amount of O_2 evolved is then:

$$O_2, \text{evolv} = O_2, \text{meas} - N_2, \text{meas} \cdot \left(\frac{O_2}{N_2}\right) \text{air where} \left(\frac{O_2}{N_2}\right) \text{air} = 0.27.$$

A value of 6.1 is reasonable for SRS waste solutions, which are normally 3 to 4 M NO_3^-. For these solutions, $G(H_2) \cong$ and $G(O_2) \cong 0.3$.

Ned then showed several graphs to illustrate the effect of radiolysis on the composition of solution with irradiation time. In neutral solutions, NO_3^- is converted to NO_2^- in about 300 h at a dose rate of $6.5 \cdot 10^4$ Gy/h ($6.5 \cdot 10^6$ R/h). If organics are added to the solutions, the behavior changes dramatically. For instance, Figure I.2 shows the behavior of a solution that is initially 1 M NO_3^- and 1 M acetate. In this solution, the NO_3^- and the acetate concentrations decrease rapidly, while the NO_2^- increases and then decreases. Similar behavior is observed for other organics such as glycol.

Although all of the gases were not analyzed (at least not illustrated here), all of the organics with few exceptions produced N_2O gas when NO_3^-- and organic-containing solutions were irradiated. One of the principal organics of interest at Savannah River Plant is tetraphenylborate, which has been used to precipitate ^{137}Cs from the waste solutions.

These radiolysis experiments are continuing at Savannah River.

Radiolysis Studies at Argonne National Laboratory

At Argonne National Laboratory, Dr. Dan Meisel is being funded by Westinghouse Hanford Company to study the radiolysis chemistry in typical simulated waste solutions. Dan and his coworkers had just received their funding and had not performed many experiments on which to report. Dan gave a brief tutorial on the chemistry of radiolysis in aqueous solutions. In an aqueous environment, there are basically three groups of radiolysis products as shown in Figure J.1. In very concentrated solutions, the reactions are expected to proceed very rapidly - on the order of 35 ps (picoseconds). In the first reaction, high energy electrons are produced which become thermalized in a matter of about 1 ps. These reactions occur in "spurs" that are about 2 nm in diameter and have a volume of about 4 nm^3. Even though the numbers of charged species that are generated by radiolysis is very small, the volumes in which they are generated are also very small. Therefore, the effective concentrations are relatively high - on the order of 1 M.

The consequences of the fast reaction kinetics are that most of the energy should be absorbed by the NO_3^-. There will be insufficient time for few, if any, of the reaction precursors to become solvated, and the presence of the high alkalinity, NO_3^-, and NO_2^- should minimize the production of H_2. Inhomogeneous kinetics will cause localized high concentrations of species and there will be a competition between recombination, diffusion, and scavenging. Both H atoms and H_2 should be produced in these solutions, but the H_2 will not be easily scavenged and should be produced with a G value of less than 0.06 (the number of atoms/molecules formed per 100 eV of adsorbed energy). Of major concern will be the H atoms that are easily scavenged and produced more readily (a G value of about 0.65). Dan expects that the contribution of the organics to the overall radiolysis reaction to occur within the "spurs."

Dan proposed a radiolysis reaction scheme in which N_2O gas would be generated from NO_3^-. The other main reaction product would be NO_2^-. [Here is another indication that the analysis of the waste

currently in Tank 101-SY, when compared with earlier analyses, will become an indicator of the reactions that are taking place.] The approach that will be used at Argonne is shown in Figure J.4.

Radiolysis Chemistry in Nitrate/Nitrite Solutions

Some of the first radiolysis experiments carried out by the Science Panel members was performed at the Risø National Laboratory in Denmark while E. J. (Ed) Hart was a visiting scientist there. Ed reported on the results he obtained during his visit to Risø and his visit to Argonne National Laboratory.

To prevent precipitation during the radiolysis experiments performed both at Risø and Argonne, Ed and his coworkers used a diluted version of the waste from Tank 101-SY (see Attachment K; K.1). In addition, there was no HEDTA available at the laboratory, so the experiments were carried out using EDTA. The results from these experiments were reported in the minutes from the last meeting (Strachan and Morgan 1991) and are summarized on K.1. Of note is the very high "G-value" for N_2O in the presence of EDTA (G_{N_2O} = 0.15) relative to the "G-value" for H_2 of 0.013. Ed and his coworkers ran the Danish code CHEMSIMUL for the mechanism on K.2, the output of which is shown on pages K.3 and K.4. The code was used to simulate the effect of gamma on the composition of the waste for the years 1980 to 1982. The results are summarized on page K.1. If these results are indicative of the reactions that are taking place in the tank, then the chemical analyses should reflect increased NO_2^- concentrations.

Ed also performed some experiments aimed at obtaining information on the formation of the crust on the waste in Tank 101-SY. In these experiments, Ed used an atmosphere of air plus 8% CO_2. This atmosphere yielded a crust on the simulated waste within 24 h and considerable water loss even though the waste was diluted relative to the waste found in the tank. In a second experiment, Ed tried to slow the loss of water from the waste solution being tested by saturating the flowing gas with water and removing the CO_2. The result of this experiment was that no crust formed after several days and no water was lost. The crusts that were formed in these experiments are shown in Figure K.5.

Ed also performed some experiments at Argonne National Laboratory. These experiments were performed using a ^{60}Co gamma ray source. The results from these experiments are shown on K.6. In these tables, "CA" stands for citric acid, "GA" stands for glycolic acid, and the other numbers such as 1674 in "#1" refer to the dose to the sample in "krad." These results indicate that with dilution there will be an increase in the H_2 production. From all samples, H_2 and N_2O were generated. At Argonne National Laboratory, HEDTA was available and the yield of N_2O was greater in these solutions than H_2. A summary of the results of the experiments performed at Argonne is shown on K.7. In this summary, "Y" is the yield of the particular gas species in μmol/L and the "G-value" is calculated by multiplying the yield by 0.964.

Ed concluded that the "G-value" for H_2 in the waste tank must be about a factor of 500 lower in the tank than the value measured in the pulsed radiolysis experiments. From this conclusion and the suspected scavenging reactions for H atoms, he also calculated that the contribution to the spur H_2 generation by radiolysis in EDTA-containing solutions is negligible. From these results and the results of some brief thermal experiments, Ed concludes that the thermal portion of the gas generation in the tank is about 30%. [This was calculated based on an activation energy of 14400 cal/mol. The activation energy measured by Delegard (1980) and by Duane Siemer (see above discussion) was 23000 cal/mol. Using the larger value for the activation energy and the remainder of Ed's numbers would mean that the thermal contribution is 12% instead of 30%.]

Ed suggested new reactions that can be added to the mechanism on page K.2. For some of these reactions (K.9), the rate constants need to be measured.

[One of the important issues here is that Ed finds N_2O is generated at a much greater rate by radiolysis of EDTA-containing solutions. The rate at which N_2 was generated by these same reactions was not measured. As noted above by Gene Ashby and coworkers, N_2 and N_2O gases seem to be generated in a 1:1 ratio, suggestive of a single mechanistic pathway. Ed, however, has analyzed the October 1990 analytical data for the gas evolved from Tank 101-SY and found that the ratio of H_2/N_2O was invariant at 1.24 as was the ratio of Ar/N_2 at 0.012. This suggests that the H_2 and N_2O are evolved together, whereas the N_2 is from the air.]

[If the same ratio is found in the planned radiolysis experiments as found in Ed's experiments and the tank gases, radiolysis would appear to be the generator ot most of the gases, since the composition of the gases generated in the Delegard's (1980) experiments seems to be quite different from the composition observed in the tank.]

Day Two of the Meeting

Before introducing the ferrocyanide issues, Thom Dunning started a discussion of information from the previous day (February 7). There was some discussion about the mechanism by which the crust is formed and the role it plays in the physical mechanism. Although the majority of the Science Panel members disagree, Ed Hart is of the opinion that the major problems in Tank 101-SY result from the presence of the crust. In his opinion, the crust ought to be dissolved. Bill Thompson warned that removing the crust would might cause major problems because the crust is thought to act as a throttle and as such it tends to limit the concentration of released gases in the tank plenum. As noted before, we need to proceed with caution. Remediation strategies suggested without the information on the chemical and physical processes could create more problems than the suggestions attempt to solve.

The need for physical modeling was discussed. It is the general feeling that the information obtained from the core samples will be insufficient to answer all of the questions needed for a basic understanding of the physical processes taking place in the tank. Therefore, it is imperative that physical modeling begin now rather than waiting until sufficient core samples are obtained to answer the majority of the questions. [Physical modeling means the use of small vessels that are constructed to study various aspects of the physical hold up and release of the gases. This differs from physical simulations, which are obtained by using a mathematical representation of the physical process in a computer code and a computer to graphically illustrate the results of the calculation.] The use of these physical models will further our understanding of the possible physical processes taking place in the tank. Dan Reynolds, Don Trent, and Bill Thompson will meet to discuss the approach. This may lead to a task in a proposal from R. T. Allemann (PNL), who is currently working on the physical processes in Tank 101-SY.

A summary of the meeting on February 7-8 will be completed on February 11 and sent to Mr. John Deichman (WHC) and Mr. John Tseng (DOE/HQ). This summary will be brief and consist of bulleted items. [This summary was written and distributed and is attached as Attachment L.]

Ferrocyanide Issues

It was expected that Mr. John Tseng would be present to introduce the Science Panel to the ferrocyanide issues, but he could not attend. In his stead, L. G. (Larry) Morgan introduced the ferrocyanide issues and why the Science Panel is being requested to consider the chemistry and physics associated with this unique waste. Larry indicated that, as is the case with Tank 101-SY, the tanks containing ferrocyanide represent an unresolved safety issue. The manner in which the ferrocyanides were precipitated yielded an oxidant (the nitrate and nitrite portions of the waste) and fuel (ferrocyanides) in an intimate mixture. Calculations indicate that this mixture could be explosive and that sufficient energy would be released during an explosion to cause significant dose to the workers in the area and to the individuals near Hanford.

During the early 1950s, the ferrocyanide process was used to process wastes and remove the ^{137}Cs. The chemistry of the process is discussed more thoroughly below. During this campaign, more than 1000 moles of $K_2NiFe(CN)_6$ (ideal compound) was produced in about 23 tanks at the Hanford Site. The process by which these wastes were processed is well documented; the identity of the solids that were produced is not well known. It is difficult to determine which processes were proposed and/or actually used. Therefore, to proceed with the project at all, the waste tanks need to be sampled. However, the same safety issues that need to be resolved in order to take a core sample from Tank 101-SY also need to be resolved to sample the waste in these tanks. The potential for an explosion is at the heart of the issues for these tanks; it is known that these materials (ferrocyanides) react vigorously, but it is uncertain if the reactions can be classified as explosive.

Larry recommended that the Science Panel review the existing information and produce a document similar to the document written for Tank 101-SY (Strachan, Reynolds, Siemer, and Wallace 1991). The Science Panel members should also review the joint PNL/WHC study plan. Lastly, he recommended that the Science Panel members study the ferrocyanide chemistry so that they can better deal with the issues associated with this waste.

The Ferrocyanide Process

Since most of the members of the Science Panel were unfamiliar with the process used at Hanford in the early 1950's, D. A. (Dan) Reynolds gave a brief history of the processes that were used at Hanford for processing spent reactor fuel to recover Pu. In particular, he covered the background to the processes that led to the generation of the "ferrocyanide" wastes (see Attachment M).

As shown in Attachment M, the first processes to separate Pu from U did not recover the valuable U and the processes were precipitation processes. It was soon realized that the valuable U could be recovered, and a new solvent extraction process was developed. During the process of recovering the U, large amounts of liquid waste were generated from which the ^{137}Cs was subsequently removed using the ferrocyanide scavenging process. In this process, potassium ferrocyanide $[K_4Fe(CN)_6]$ was added to the acid waste, the solution pH adjusted to 9 ± 1, and adding equal molar $NiSO_4$. This process was supposed to precipitate $Cs_2NiFe[CN]_6$, but the ^{137}Cs was probably carried down as a solid solution with some other alkali-nickel ferrocyanide.

Since the major concern was precipitation of the ^{137}Cs, no effort was made to fully characterize the waste resulting from the ferrocyanide waste. Instead, the waste was allowed to settle for several days, and

the supernate was pumped to a crib [a covered ditch in the sand], while the solid remained in the tank. The waste supernate was checked for radioactivity before being pumped, but no other analyses were performed. Similarly, the solid waste in the tank was not analyzed.

The flow sheet for the ferrocyanide precipitation was changed over the period in which it was used. In the beginning, the potassium salt was used, but later the less expensive sodium salt was used. Calcium nitrate and, later, $Sr(NO_3)_2$ were added to improve ^{90}Sr removal. The concentrations of $Na_4Fe(CN)_6$ and $NiSO_4$ were reduced by a factor of two. Before the end of the campaign, Na_2HPO_4 was added to wastes low in PO_4^{3-} to improve the sorption on the soil.

Over the years since these wastes were generated, these tanks were used for other wastes either temporarily or permanently. Some of these wastes were highly alkaline and may have caused partial dissolution of the ferrocyanide solids, although this has not yet been confirmed. It is the addition of these other wastes, a major source of the nitrates and nitrites, that is the cause for major concern. Use of single-shell tanks was discontinued in the late 1970s. All of the pumpable liquids have been removed from these tanks and now reside in the double-shell tanks. Although some of these tanks continue to be pumped using low volume pumps, some liquids cannot be removed because they are held by capillary forces.

Further information and a sample ferrocyanide flow sheet are found in Attachment N.

Ferrocyanide Chemistry

If the ferrocyanide product is not well documented, the properties of the ferrocyanide product are less well known. Dr. L. L. (Lee) Burger has worked for several years on the chemistry associated with the ferrocyanide products. He presented what is known about the chemistry of the ferrocyanide process. His presentation is included as Attachment O.

From what can be gleaned from the early Hanford documents, the most probable conditions and products are shown in O.1. Because of the very low molar concentration of Cs in the wastes, there is little likelihood that the pure compound $Cs_4Fe(CN)_6$ exists in the waste tanks. Since there are no thermodynamic data on the ferrocyanides, Lee estimated the heat of reaction (ΔH) using other compounds (O.2). Similarly, Lee estimated the heats of formation (ΔH_f) for $Ni_2Fe(CN)_6$ and $Na_2NiFe(CN)_6$ using the ΔH_f's of other cyanides.

Lee and his coworkers have calculated from thermodynamic data the energy released during exothermic reaction between $NaNO_3$, $NaNO_2$, and $Na_2NiFe(CN)_6$ and have compared these energies to the energies released during the explosion of several known explosives. Data were also obtained from scanning calorimetry experiments. The energy released in the reaction of $NaNO_3$, $NaNO_2$, and $Na_2NiFe(CN)_6$ is somewhat lower than for other explosives. Also, less gas is released during the ferrocyanide reaction. As part of the ongoing safety studies, experiments are being carried out at Los Alamos National Laboratory to measure more accurately the energy of the reaction and evaluate the sensitivity of the mixture. As part of this study, larger batches of the mixture will be studied, since heat losses to the environment can quench the reaction sufficiently to keep the reaction from becoming self propagating.

In Figure O.6, a typical scanning thermogram and differential scanning thermogram are shown. This thermogram is for a mixture of a ferrocyanide and $NaNO_3/NaNO_2$ that was first mixed wet and then dried at 100°C before the thermogram was made. Figure O.7 shows the differential scanning calorimeter (DSC)

for the oxidation of two dry ferrocyanide salts in air. This thermogram differs from the oxidation of the salts in the presence of $NaNO_3$ and $NaNO_2$. The difference between the materials produced in "Batch 1" and those in "Batch 2" is not certain, but the order in which the chemicals were mixed to precipitate the salts in "Batch 2" was the reverse of the order when making "Batch 1." The reactions that take place in these salt mixtures depends on the composition of the salt mixture. To illustrate this effect, DSC analyses were performed using 50% $Na_2NiFe(CN)_6$ with 50% of either $NaNO_3$ or a mixture of $NaNO_3/NaNO_2$ (O.8). The results from this DSC indicate that the reaction temperature is shifted to lower temperature when $NaNO_2$ is present. Increasing the amount of oxidant present above the stoichiometric amount decreases the magnitude of the exothermic energy release. For comparison of materials, it is also important to fix the heating rate at which these analyses are made. In Figure O.10, Lee showed that as the scan rate increased, the temperature at which the exothermic peak occurred also increased for $Cs_2NiFe(CN)_6$. This information can be used to obtain the activation energy (E_a) for the reaction.

Lee and his coworkers have performed a number of time-to-explosion (TTX) experiments. In these experiments, a small (≈40 mg) amount of salt mixture is loaded into an NMR tube [a thin-walled small glass capillary tube] and the tube placed in a heated metal block. The time needed for the mixture to explode is recorded as a function of the temperature of the preheated metal block. Results from a set of typical TTX experiments with a mixture of $Cs_2NiFe(CN)_6$ with a mixture of 65 wt% $NaNO_2$ and 35 wt% KNO_2 is shown in Figure O.11. Minimum temperatures of about 300°C are required for the particular mixture shown in Figure O.11 to explode. Figure O.12 shows the sensitivity of the time to explosion temperature to the composition of the salt mixture. The upper curve in Figure O.12 is for $Cs_2NiFe(CN)_6$. Adding an organic such as ethylenediaminetetraacetate decreases the time to explosion. The remaining curves in Figure O.12 are for various precipitates of nickel ferrocyanides including a commercial $Ni_2Fe(CN)_6$ (Pfalz and Bauer). Oxidizing the Fe(II) to Fe(III), i.e. producing the ferricyanide, appears to lower the temperature at which these compounds explode, but the data are incomplete and more data need to be collected to draw a firm conclusion. The above results are reinforced by the results tabulated on page O.14. In the experiments summarized in this table, the compound being studied was mixed with the oxidant shown in the table. The metal block used to heat these samples was held at a constant 360°C and the time to explosion was measured. The critical explosion temperature (T_c), determined from other experiments, is also listed.

From the above-mentioned experiments, Lee and his coworkers have been able to estimate the activation energy of the oxidation reaction for $Cs_2NiFe(CN)_6$. The experiments that were used to determine the activation energy were the DSC and the time-to-explosion tests carried out under isothermal conditions. The DSC work is shown in Figure O.10 and discussed above. The isothermal experiments are discussed in the previous paragraph. This result allows one to calculate the rate of the reaction between $Cs_2NiFe(CN)_6$ and $NaNO_3$ at any temperature over which the reaction mechanism remains the same. The activation energies for two of the ferrocyanide reactions and three known explosives are shown in the table on page O.16. These activation energies allow one to get a general understanding of the temperature sensitivity of the reactions, but these data may not be used to compare the rates at which these reactions occur, i.e. explosiveness, at any given temperature. More information is needed besides the activation energy.

Lee indicated that part of the experimental problem in working with explosives is the effect that heat loss to the apparatus and/or the surrounding material has on the results. This is illustrated in Figure O.17. In this graph, Lee pointed out that a solid can remain in thermal equilibrium with the container in which it is being tested or the surrounding material with which it is being tested if the heat generated is low relative to the rate at which the apparatus or heat sink can dissipate the heat. However, if the heat generated

becomes large with respect to the heat lost to the heat sink, then the samples become self heating and the reaction "runs away." This effect should be an important consideration when studying reactions of this nature. An example of this effect is shown in Figure O.18. These data came from an experiment in which Lee placed a small amount of a ferrocyanide and nitrate oxidizer in a 5-mm glass tube. A thermocouple was centered in the NMR tube and the temperature of the solid was measured as it was heated from room temperature to 360°C using a stainless steel block at 360°C. The time to explosion, as determined by the sharp increase in temperature recorded from the thermocouple, is much longer than the times recorded in experiments without the thermocouple present (see Figure O.14). This is because a significant amount of the heat being generated by the reaction in the sample was being dissipated through the thermocouple.

In an effort to further understand the temperature dependence of the explosion reaction for $Cs_2NiFe(CN)_6$ with a mixture of $NaNO_2$ and KNO_2, the results from the time to explosion experiments over a range of temperatures from about 290°C to 400°C were plotted as log-time vs 1/T. The results from a typical experiment are summarized in Figure O.19 and suggest a change in kinetic mechanism at a temperature of about 310°C. Since the reaction mechanism is unknown at this time, it is only possible to indicate that the mechanism changes and has a higher activation energy at the lower temperatures.

One of the concerns with the results from the experiments that have been carried out to date is that most of the experiments have been performed using more-or-less pure materials. However, in the tanks there are inert materials such as carbonates, aluminates, and water. These material are likely to reduce the energetics of any exothermic reaction through dilution and heat absorption. To estimate the effect of water, for instance, the heat of vaporization of water and the heat required to heat the water to 100°C must be provided by the exothermic reaction. In addition, the heat of melting of the salts and the heat of decomposition of the nitrates/nitrites must also be taken into account. Lee showed the calculations that must be made to perform this calculation. Estimates of the energy required to heat various compounds to three different temperatures are shown in Figure O.21. This heat requirement is then available to quench the "run away" reaction.

There has been some suggestion that the nickel ferrocyanides may be more soluble in highly alkaline solutions. Lee listed some of the stability, dissociation, and solubility constants for some of the chemical species in the $Ni\text{-}Fe\text{-}CN^-\text{-}OH^-$ system. These constants can be used to estimate the solubility of some of the ferrocyanides at different pH values. [The stability constants for the hydroxide complexes of Fe and Ni are missing from this listing and may be important in any calculation of the solubility of the ferrocyanides.] As an example, Lee calculated the change in the ratio of Fe(III) to Fe(II) cyanide complexes.

Lee also indicated that radiation chemistry is probably also very important. He listed some of the reactions that were listed by Ed Hart earlier plus some others. These chemical species generated by the radiolysis events may, and probably will, play an important role in the oxidation of ferrocyanide to ferricyanide. Other reactions may also be important, such as reactions between radiolytically generated specie and the cyanide ligand. The system is complex and will require a comprehensive experimental program.

Lee concluded with a brief discussion of the current program. This is a program with limited scope. The number of compounds being studied is limited as are the conditions under which these compounds will be studied. There are several important areas that need investigation and that are not being studied. The Science Panel will need to help identify those areas that need to be addressed to understand the chemistry of the decomposition reactions, the analytical chemistry, and the chemistry involved in the precipitation and dissolution of these compounds.

Other Discussion

The Science Panel members returned to some questions that had been sent to them by Mr. John Deichman and Mr. Jerry Johnson, both from Westinghouse Hanford Co. One question concerned the use of taking extra samples during the core drilling operation. The main thrust of the question concerned using the samples for laboratory gas generation experiments. The Science Panel members indicated that they were unprepared to determine the usefulness of performing laboratory gas generation experiments with actual samples from the tank, but there was genuine interest in obtaining extra samples so long as the taking of these samples did not interfere with the overall coring operation. If this were possible, it would mean that there would be enough sample to obtain the information critical to understanding the chemical and physical mechanisms. The priority should be given to getting extra samples from the bottom of the tank. Samples of the crust should take second priority with the liquid samples having the lowest priority.

At this point in the meeting, Thom Dunning, Larry Morgan, Ben Johnson, and Denis Strachan had to leave the room for a phone call to John Deichman and John Tseng. The remaining members of the Science Panel discussed other questions. Some notes were taken, but Denis was not able to relate them to the questions that were taken. Therefore, this part of the meeting is not recorded here. There was a general interest by the Science Panel members in the ferrocyanide waste problems and most indicated that they could be available if needed to serve on a Ferrocyanide Panel.

The Science Panel members discussed the subject of expanding the purview of the Science Panel to include the ferrocyanide issues. The Panel members agreed that the Science Panel should take on the ferrocyanide issues, but that the Science Panel should be reorganized into a panel of permanent members and sub-groups or working groups having the charter to investigate a particular issue such as ferrocyanide or hydrogen generation.

The next meeting of the Tank Waste Science Panel should be in about three months (May or June). The meeting was adjourned.

References

Strachan, D. M., D. A. Reynolds, D. D. Siemer, and R. W. Wallace. 1991. *A Survey of Available Information on Gas Generation in Tank 101-SY.* PNL-7520, Pacific Northwest Laboratory, Richland, Washington.

Mauss, B. M. 1986. "101-SY Samples: Laboratory Analysis and Results." Letter No. 65453-86-079 (to L. M. Sasaki), Rockwell Hanford Operations, Richland, Washington.

Delegard, C. 1980. *Laboratory Studies of Completed Waste Slurry Volume Growth in Tank 241-SY-106.* RHO-LD-124, Rockwell Hanford Company, Richland, Washington.

Strachan, D. M. and L. G. Morgan. 1991. *Minutes of the Tank Waste Science Panel Meeting September 13-14, 1990.* PNL-7599, Pacific Northwest Laboratory, Richland, Washington.

Strachan, D. M., R. D. Lokken, R. D. Scheele, and A. P. Toste. 1986. *Complex Concentrate Pretreatment. FY 1986 Progress Report.* PNL-7687, Pacific Northwest Laboratory, Richland, Washington.

ATTACHMENT A

AGENDA

TANK WASTE SCIENCE PANEL MEETING
FEBRUARY 7 & 8, 1991
REGISTRY HOTEL
DENVER, CO

THURSDAY, FEBRUARY 7 (Room to be displayed on the reader board)

8:00	Breakfast (served in the meeting room).
8:30	Introductions and Introductory Comments - TH Dunning Request from Robert Marusich
9:00	Thoughts on the Kinetics of Gas Generation and Crust Formation in Tank 241-SY-101 - DM Strachan
10:00	Break
10:15	Data from the October 24, 1990 Gas Release Event - DA Reynolds DL Herting
11:00	Hydrogen Production from Organics and the Detection of Trace Quantities of Hydrogen - DD Siemer
12:00	Lunch (served in the meeting room).
12:30	Presentation of Radiolysis Work at Savannah River - NE Bibler
1:00	Radiolysis Chemistry in Nitrate/Nitrite Solutions - EJ Hart
2:00	Chemical Mechanisms Studies at Georgia Tech - EC Ashby
3:00	Break
3:15	Radiolysis Studies at Argonne National Lab - EP Horwitz
4:00	Discussion

FRIDAY, FEBRUARY, 8 (same room)

8:00	Breakfast (served in the meeting room).
9:00	Introductory Comments - TH Dunning
9:30	Introduction to Ferrocyanide Issues - J. Tseng
10:00	History of Ferrocyanide Process - DA Reynolds
10:45	Break
11:00	Chemistry of Ferrocyanides and Summary of the Chemistry of Ferrocyanides - LL Burger
12:00	Lunch (served in the meeting room).
12:30	Discussion of Data Needs, Plan of Attack, etc.
3:00	Adjourn

ATTACHMENT B

ATTENDANCE LIST

NAME	AFFILIATION
S. Agnew	Los Alamos National Laboratory
E. C. Ashby	Georgia Institute of Technology
N. E. Bibler*	Westinghouse Savannah River
L. L. Burger	Pacific Northwest Laboratory
T. H. Dunning, Jr.	Pacific Northwest Laboratory
E. J. Hart	Consultant
D. L. Herting	Westinghouse Hanford Company
E. P. Horwitz	Argonne National Laboratory
B. M. Johnson, Jr.	Pacific Northwest Laboratory
D. Meisel**	Argonne National Laboratory
L. G. Morgan	Pacific Northwest Laboratory
D. A. Reynolds	Westinghouse Hanford Company
W. W. Schulz	Consultant
D. D. Siemer	Westinghouse Idaho Nuclear Co.
D. M. Strachan	Pacific Northwest Laboratory
W. J. Thompson	Washington State University
D. S. Trent*	Pacific Northwest Laboratory
H. W. Walter*	Department of Energy/HQ

* Attended the second day only.
** Attended the first day only.

ATTACHMENT C

THOUGHTS ON THE CHEMICAL MECHANISM OF GAS GENERATION AND CRUST FORMATION IN TANK 241-SY-101

D. M. Strachan

Over the past several weeks, I have been giving some thought to the chemical mechanism of gas generation and crust formation. I have summarized my thoughts below. It should be pointed out, however, that my thoughts on crust formation were catalyzed during a meeting held by Harry Babad (WHC) at which Dan Reynolds showed pictures of Tank 101-SY taken over the years since it was filled. The mechanistic model of how the crust was/is formed was given by Harry, who may or may not have been the originator. Also, Rudy Allemann's treatment of the pictures taken in 1989 of the crust in Tank 101-SY played a role in what follows.

CHEMICAL MECHANISM OF GAS GENERATION

Since Tank 101-SY was filled, waste volume readings have been taken using both an automatic Food Instrument Co liquid level gauge (FIC gauge) and a manual tape. The readings from these measurements have been recorded and the data since early 1984 are available as a Lotus 1-2-3® file. From these data I have been able to come to some conclusions that will ultimately need verification.

Figure 1 shows the typical data that are obtained from the FIC gauge. These data span the time from March 1984 to December 1990. Upon first glance, it appears that an analysis of these data would at best be fraught with large uncertainties. However, one can see that the data appear to be more manageable when one looks only at the time between gas release events (Figure 2). Even these data do not appear to lend themselves to analysis largely because of the "mini burps" between the larger burps. However, by removing these small fluctuations from the data - in effect making the assumption that the burps are due only to physical phenomena - the data become amenable to analysis (Figure 3). To remove these mini burps from the data, the height lost during a mini burp is added to the recorded heights after the small release and the time over which the small release event occurs is subtracted from all of the times after the event.

A linear increase in waste volume with increasing time is indicated by these data (Figure 3). Furthermore, all of the data analyzed to date appear to indicate a linear increase in volume as a function of time. The slope or rate of gas generation varies depending on the time since the waste was placed in the tank and if "lancing" was being performed. One period between gas release events was selected from each year and treated in a similar fashion as

described above (Figures 4 to 9). In all cases the fit of the data to a straight line was excellent with a relative standard deviation of about 5% or less.

Since each of these plots is linear, once must conclude that the rate is independent of the mechanical stirring of the tank during a release event, the gas generation rate is independent of the mechanical processes, and the rate is insensitive to the increase in temperature that occurs between events. A chemical event that is linear in time indicates that the system is at steady-state, or the reaction is zero order, or the concentration of the rate limiting species is at steady-state. It also indicates that the reaction is independent of the H_2 and the N_2O partial pressures. In the case of N_2O, the relative saturation of this gas in solution may be constant before and after a gas release event, so the concentration appears to be at steady-state as far as the chemistry is concerned.

Since the slope of the lines in Figures 3 to 9 should be the rate at which the gas is being generated, the time variance of the slope might indicate something about the primary source of the gases. To investigate this aspect of the data, I plotted the rate (slope of the line) against the time since the first available data (Figure 10). If the rate were dependent on the activity of ^{137}Cs or ^{90}Sr then the decrease should follow an exponential decay from the first data point to the last. (The half lives of the two isotopes are nearly equal: ^{137}Cs = 30.23 years and ^{90}Sr 28.1 years.) There are insufficient data to validate the conclusion that one of the rate controlling steps is the amount of activity, but the interpretation is at least consistent with the data. Earlier, I though there might be an indication that air lancing in the tank significantly increased the rate of gas generation. However, including data earlier than 1984 significantly increased the noise in the data so as to obscure any effect of air lancing on the gas generation rate. A statistical approach may allow us to make more firm conclusions on the effect of air lancing. From our brief experience in the laboratory, we know that O_2 is needed for the reaction. A least squares fit of the data to the equation $y = A \cdot \exp(-6.296 \cdot 10^{-5} \cdot t)$ yielded a value for A with a standard deviation of less than 3%. This line is shown in Figure 10.

CRUST FORMATION

Up until recently, I was a strong believer that the gas was diffusing through the crust once it had been released from the bottom of the tank. In fact, one cannot rule out this mechanism because reasonable permeabilities are calculated from the volumes of gases released and the time over which they are

released. However, other physical evidence would argue that this mechanism may play only a partial role in the release of gases from the waste.

A figure from Allemann et al (Figure 11) and their analysis of this figure indicates that the liquid waste from below the crust is pushed onto the top of the crust during an event. This is deduced from the general appearance of the crust and the displacement of cables and pipes that have been in or on the crust for a long period of time. This physical model of the crust suggests that the waste is preferentially released from one direction and either flows out on top of the crust or causes a displacement of the crust such that the dark material is replenished while the white material is not and may be very old crust.

Three pieces of information are consistent with this model. One piece of information is the recent chemical analysis of the samples taken from the top of the crust. Results from these samples suggest that the composition of the dark material from the crust is similar to the composition of the liquid waste that was analyzed in 1986 by Mauss.

The second piece of information consistent with this model of the crust formation are the gamma scan data, which indicate a high concentration of gamma activity at the same level as the crust. If the liquid waste was being forced onto the top of the crust, then one would expect the ^{137}Cs activity to be high - certainly higher than expected if the model was that the crust formed from the reaction between air and the highly alkaline liquid. The old part of the crust - the white part - would be expected to contain less ^{137}Cs and more carbonate. It is known from the analysis of the recent samples that this material is much drier than the samples of dark material.

The third piece of information that is consistent with liquid waste flowing onto the top of the crust is the low level readings obtained using the manual tape. The manual tape is on the opposite side of the tank along a diagonal running through the position of the FIC gauge and the center of the tank. This device is located in the area of the predominantly white material. The waste level readings are consistently less than the FIC gauge readings by about 20 inches. This discrepancy has always been puzzling, but would be explainable if the major portion of the crust formed by liquid being ejected from below the crust to the top of the crust.

To pursue this latter point a bit further, I plotted the difference between the FIC readings and the manual tape readings against the time since the tank was filled (Figure 12). To save time, I randomly selected pairs of height measurements each month. When there was liquid in the tank, first data point,

the readings should be equal, zero on this plot. However, within four months the difference became negative; the FIC gauge readings were less than the manual tape readings. What I think this means is that a crust began to from in the area of the manual tape during the first four months after adding the first waste to the tank, even though there were three addition of waste during that time period. The last waste to be added to the tank was in November 1980, about 900 days in Figure 12. The four data that are positive appear to be the result of flushing of the FIC or manual tape, change out of these devices, or malfunctions; they do not appear to be related to waste additions. Probably the most interesting trend in the data, however, is the trend toward zero from about 1200 days to the latest data that I had which is for March 1984. The data used in the analysis of the kinetics (Figures 1 to 10) contained only the FIC gauge readings. Mr. Dan Reynolds (WHC) is sending me the remaining data I need to complete this analysis. However, it is important to note that recent data show the difference between the FIC and the manual tape at about +20 inches. In December 1990, the FIC and manual tape were replaced and calibrated. The levels made after installation of this equipment reproduced the data taken with the equipment that had been removed. Thus, the difference in waste heights measured earlier is accurate and from about February 1984 the crust on the side of the FIC gauge became thicker with time as waste was added to the top while the crust on the manual tape side remained constant or did not increase in thickness at the same rate as the dark portion. It should be noted that the sample obtained from the manual tape in December 1990 was "dry" and sparse which is consistent with the model of the crust proposed here. Also, some people think that the crust is tilted; this model would suggest otherwise.

FUTURE WORK

I have only analyzed a fraction of the available data. Data from 1978 to 1984 exist, but in hard copy rather than magnetic. A cursory look at these data suggest that the rates of gas generation are consistent with those that would be predicted based on ^{137}Cs decay. These early data need to be treated in a similar fashion as I have done above. However, Larry Pederson suggested that, rather than manipulate the data as I have done, the data should be treated statistically to determine if the mechanism I propose is valid.

In looking at the data for the time period between 1978 and 1984, I have noticed that the "modern day" burps only started after the last waste was added to the tank in November 1980. Before this time the cycle from low waste volume to high waste volume was about 2". This would indicate that there was

something special about the last waste. I have requested this information and hope to find something unique about this waste that could be linked to the gas generation in this tank.

THOUGHTS ON THE MECHANISM OF GAS GENERATION IN TANK 241-SY-101

DENIS STRACHAN

TANK WASTE SCIENCE PANEL MEETING
FEBRUARY 7 & 8, 1991
DENVER, CO

THOUGHTS ON THE MECHANISM OF GAS GENERATION IN TANK 241-SY-101

D. M. STRACHAN

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

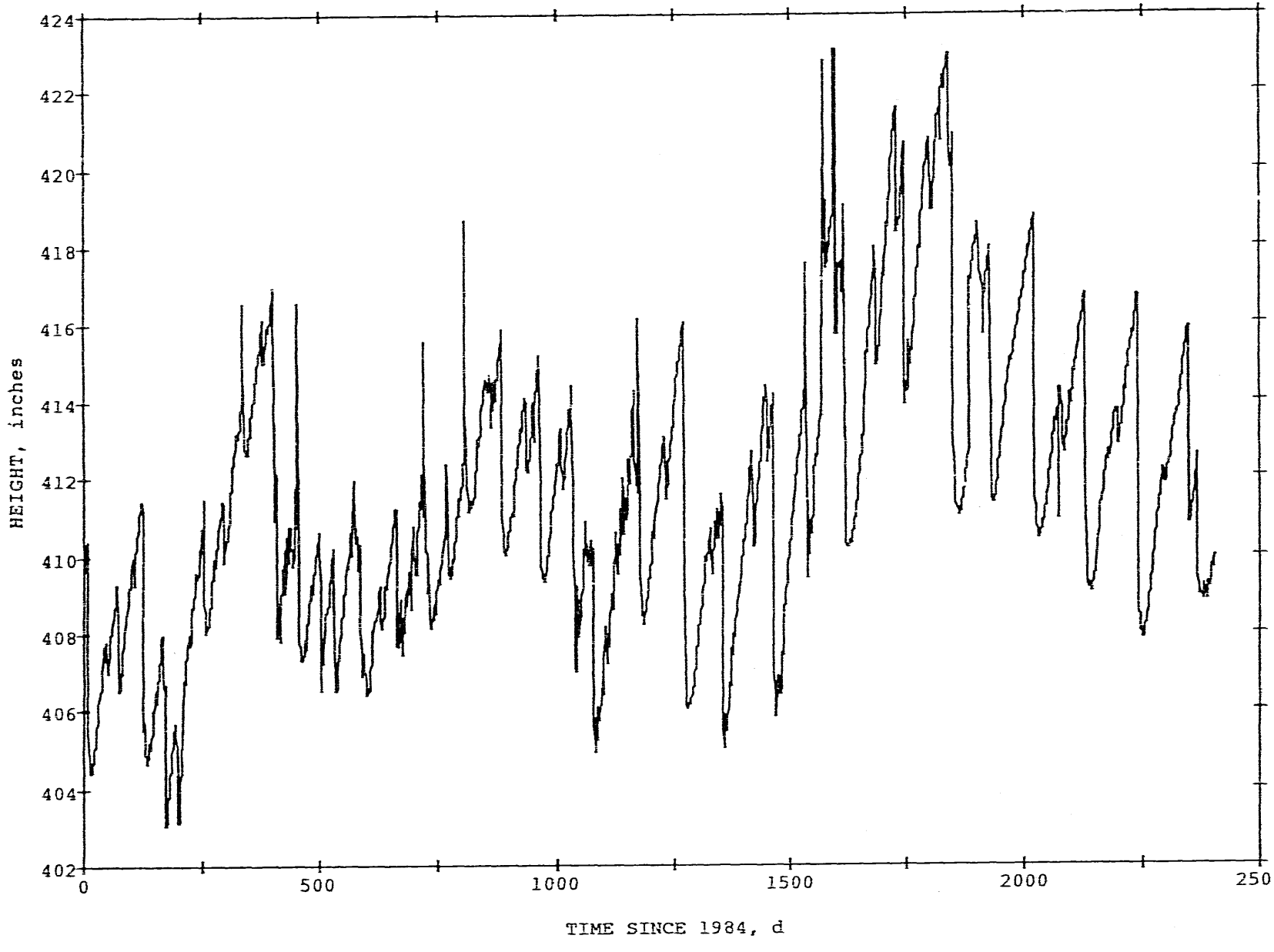
MARCH 12, 1991

RICHLAND, WA

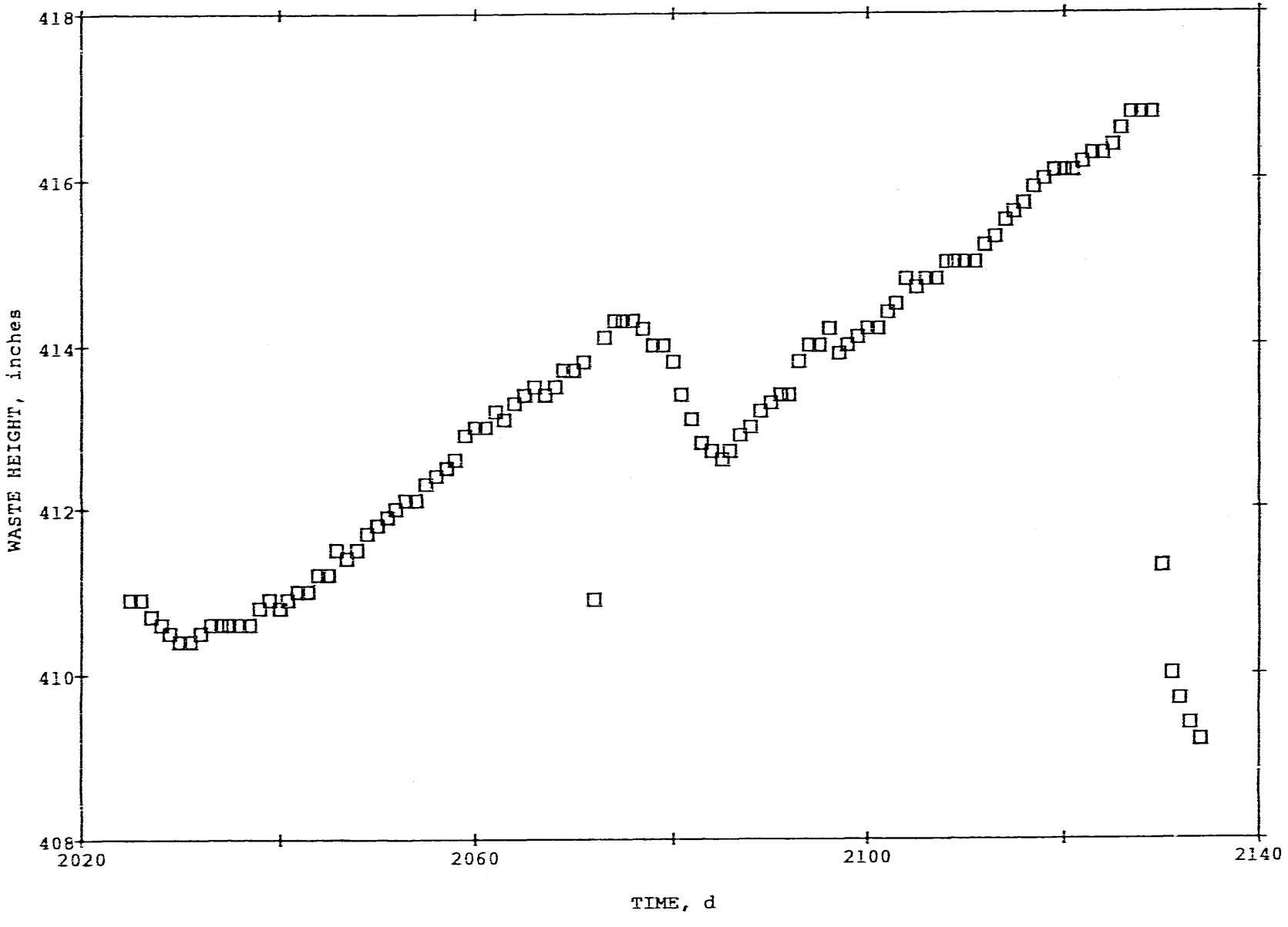
REVIEW OF TANK WASTE HEIGHT DATA

- DETERMINE KINETIC PARAMETERS
- DETERMINE CRUST FORMATION MECHANISM

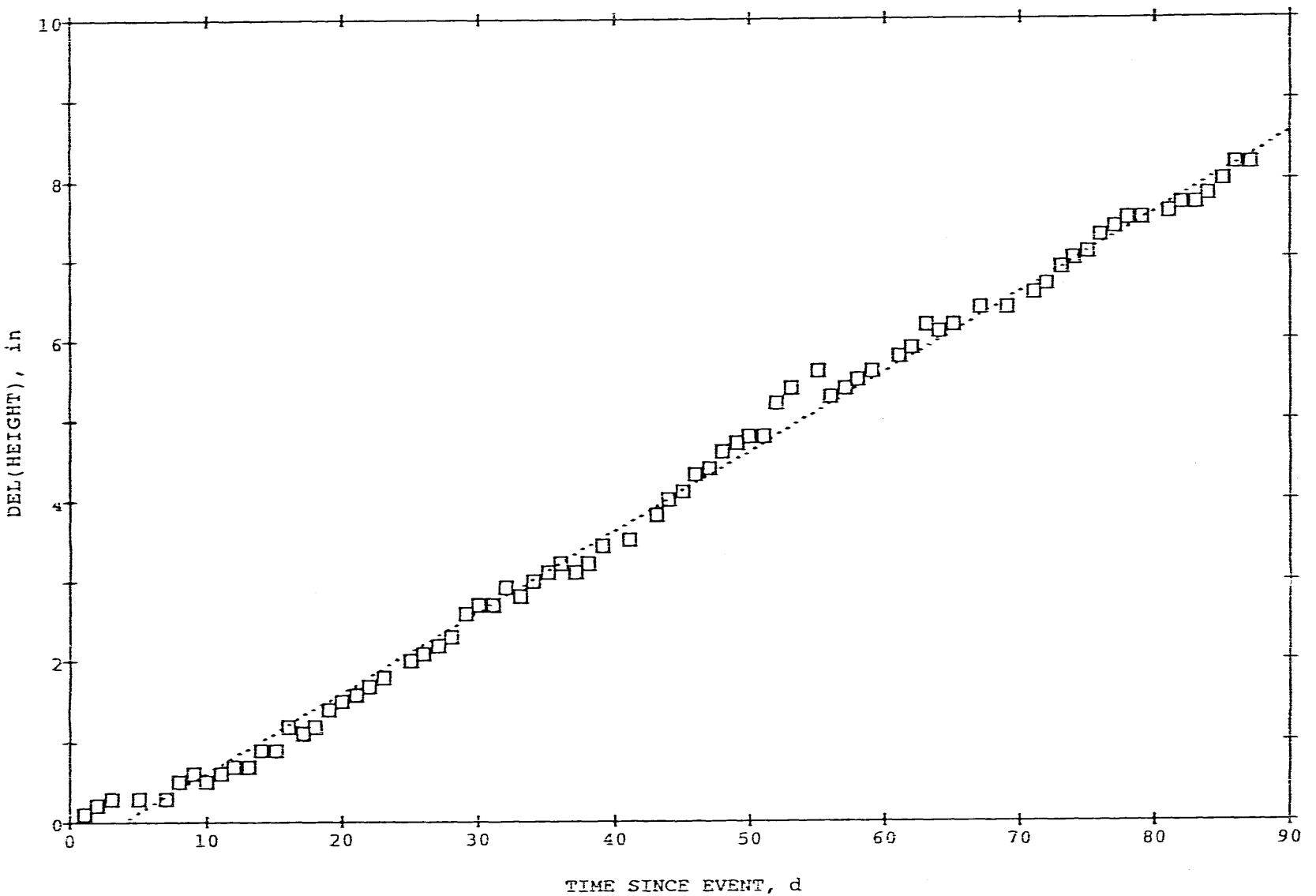
WASTE VOLUME DATA FROM THE FIC GUAGE IN TANK 241-SY-101



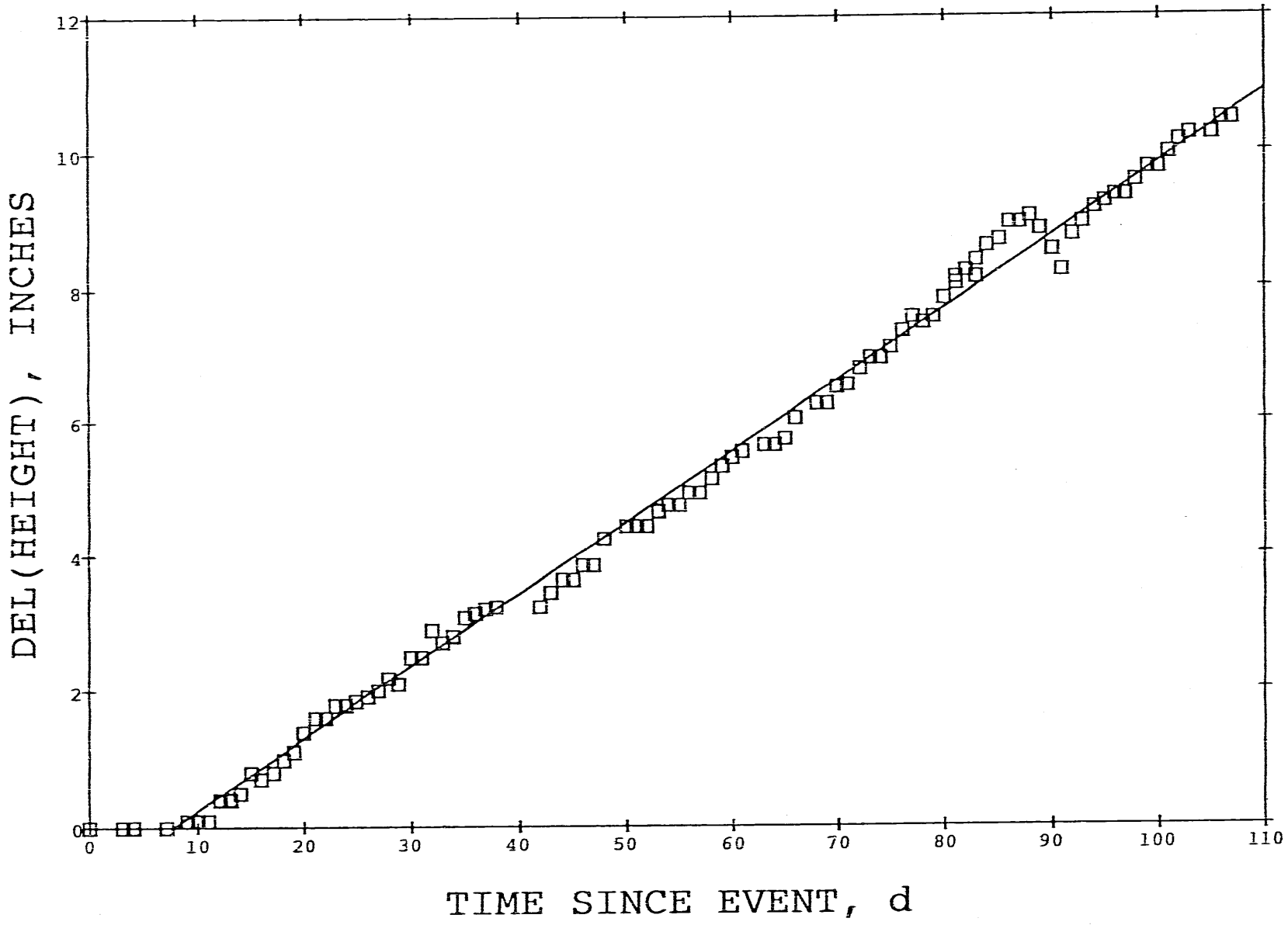
SAMPLE DATA FROM TANK 241-SY-101
TANK LEVEL DATA FROM SEPTEMBER 16, 1989 TO DECEMBER 31, 1989



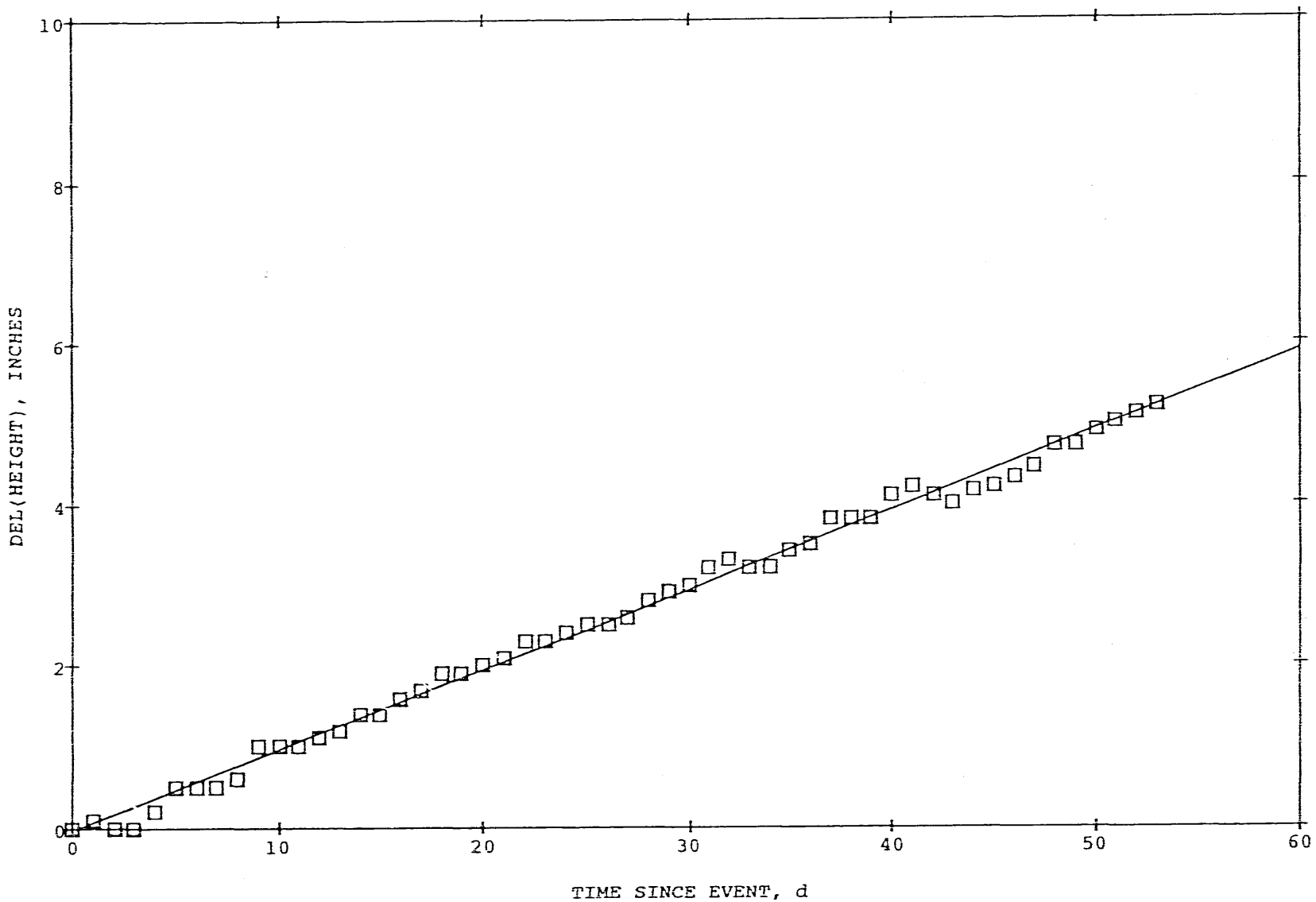
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP FROM SEPTEMBER 21, 1989 TO DECEMBER 29, 1989



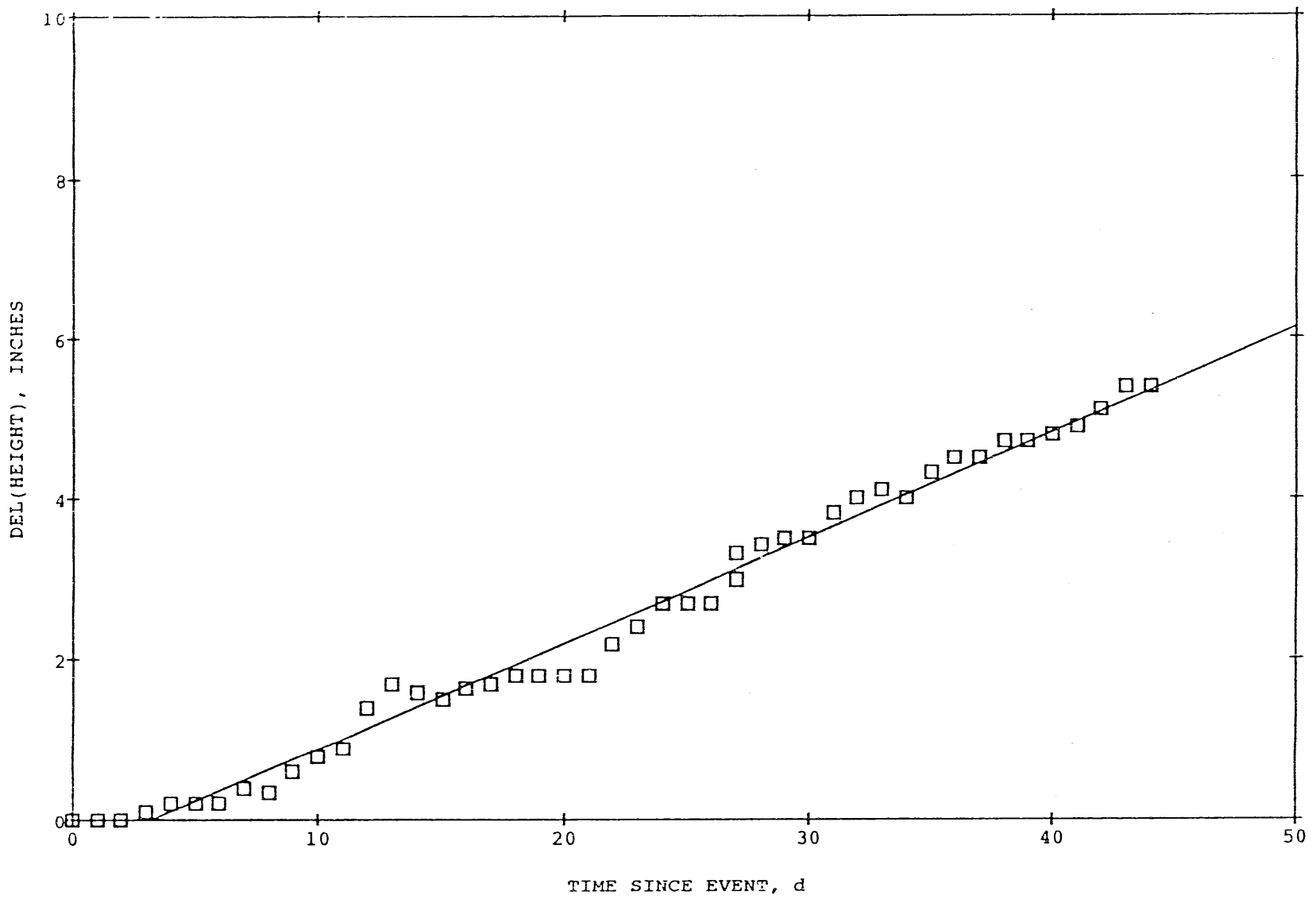
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
IN TANK 241-SY-101 FROM MARCH 13, 1984 TO JULY 3, 1984



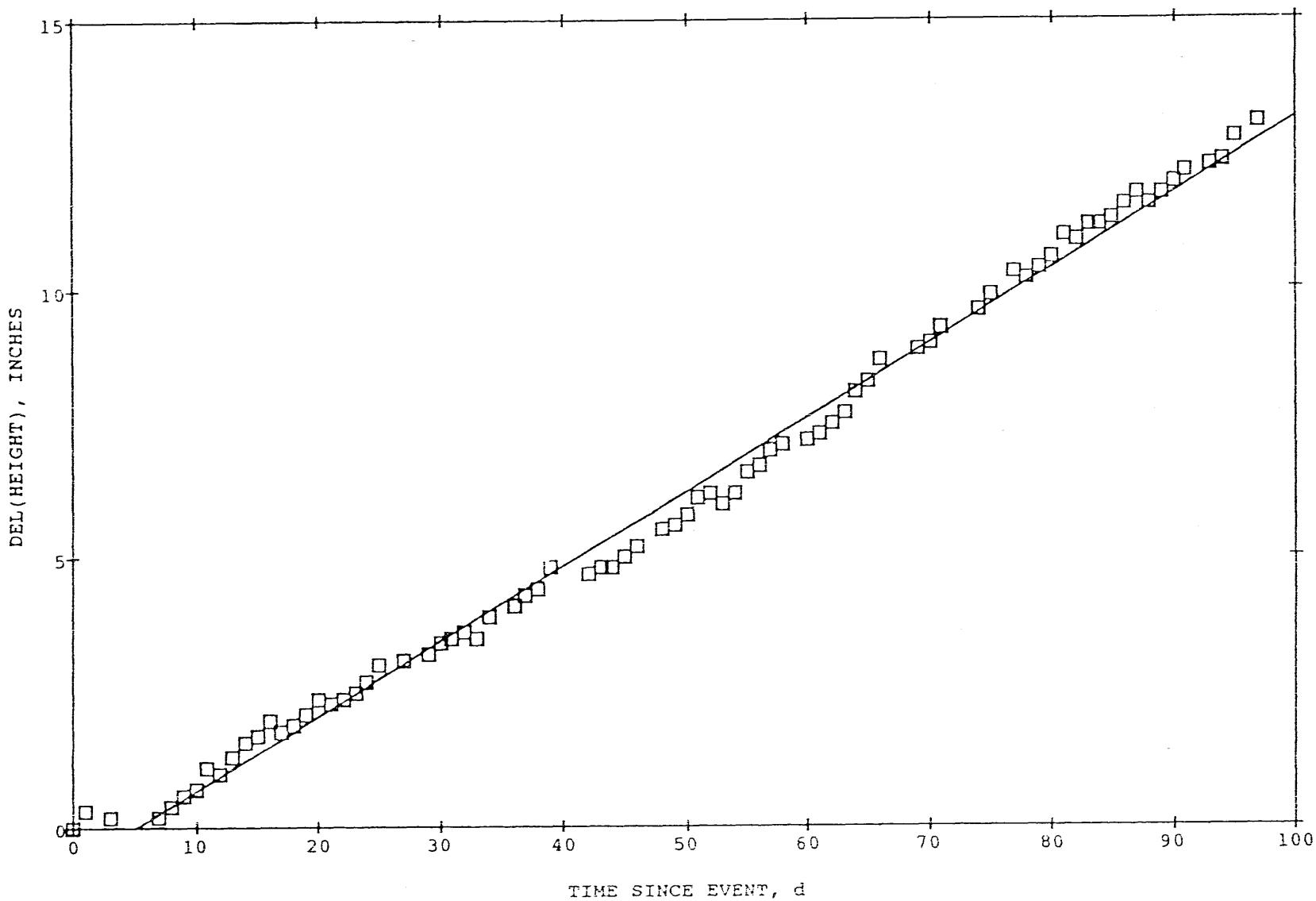
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
N TANK 241-SY-101 FROM FEBRUARY 10, 1985 TO APRIL 8, 19



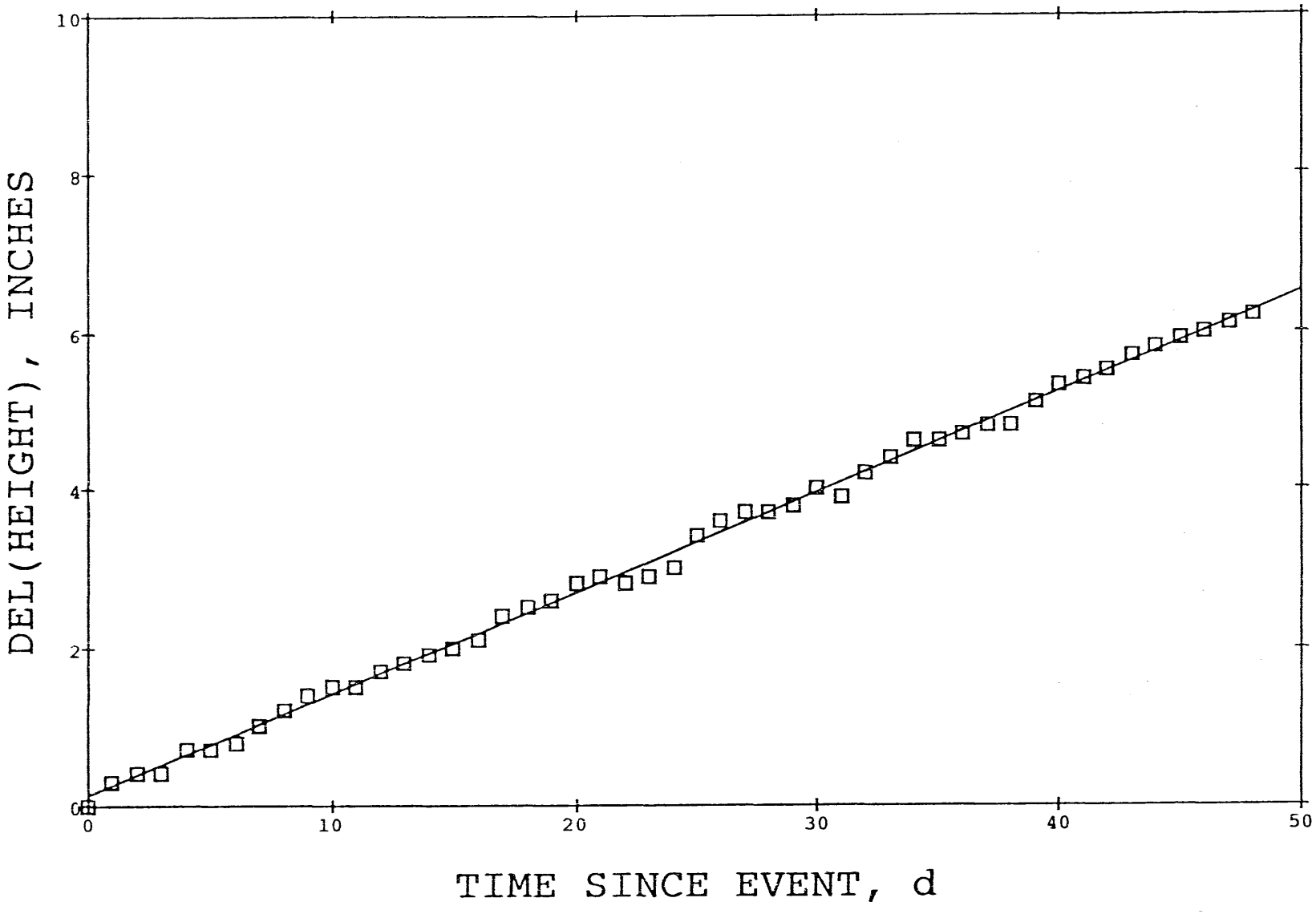
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP IN TANK 241-SY-101 FROM MAY 31, 1986 TO AUGUST 3, 1986



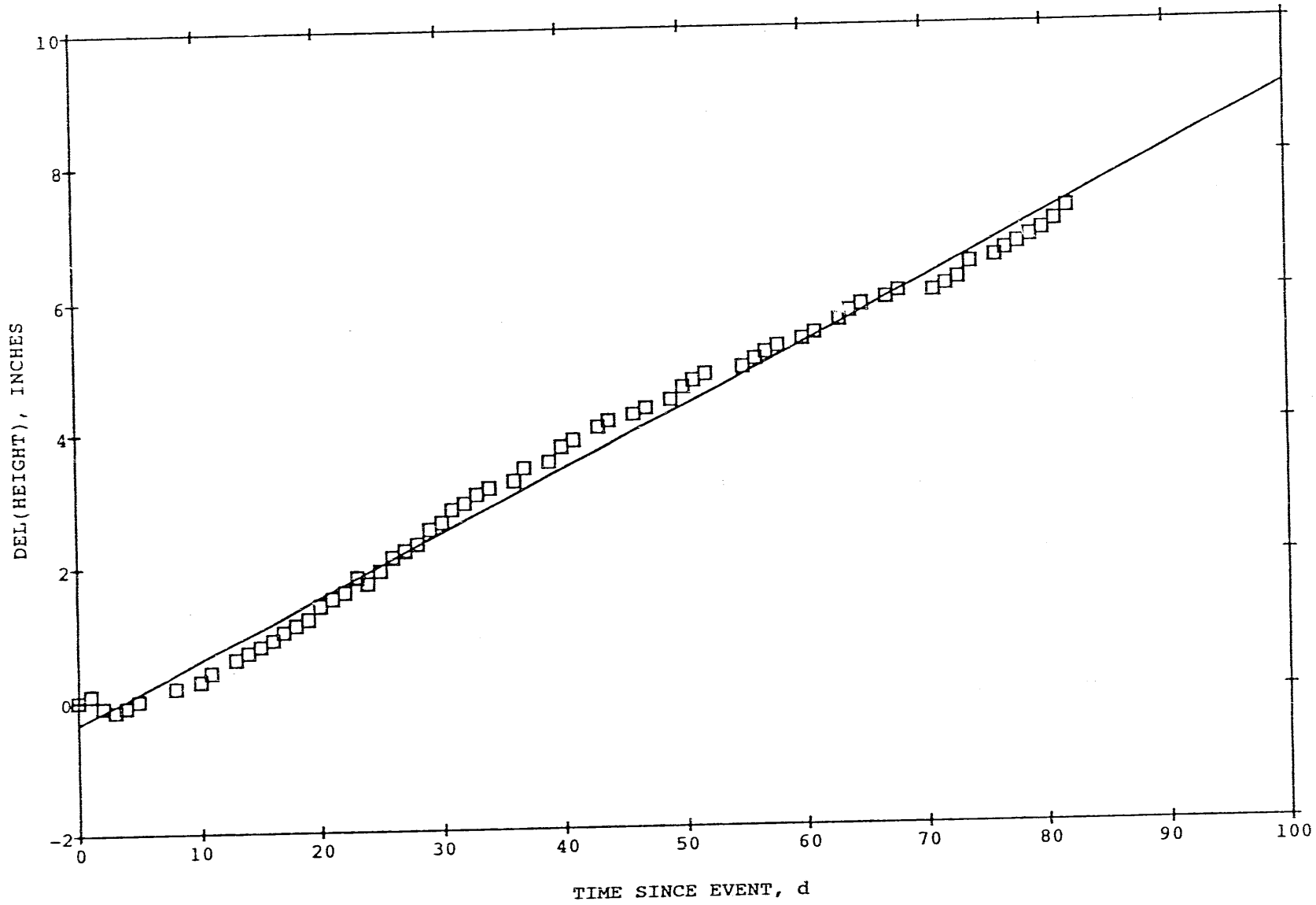
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
N TANK 241-SY-101 FROM NOVEMBER 20, 1987 TO MARCH 4, 19



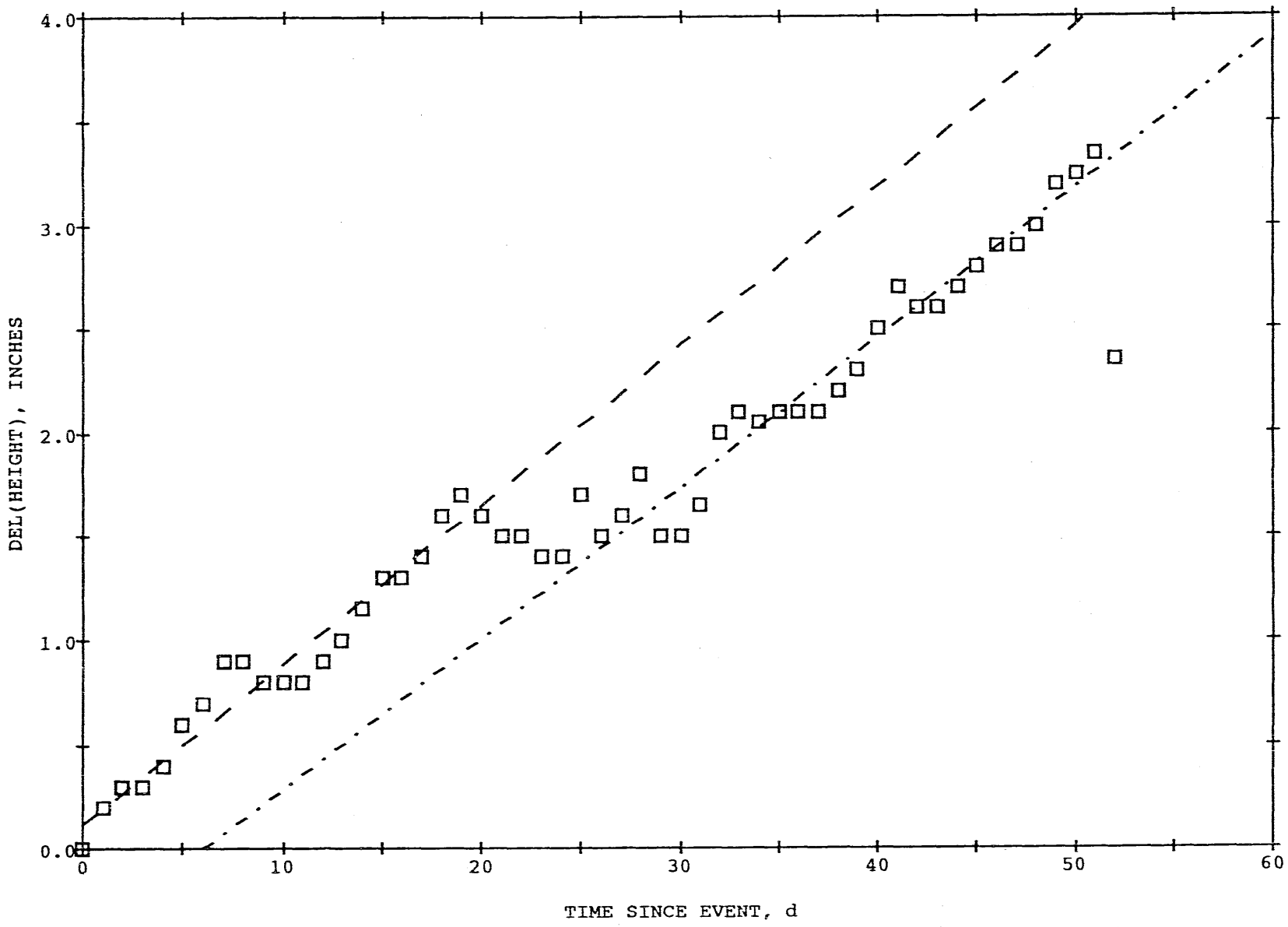
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP IN TANK 241-SY-101 FROM MARCH 25 1988 TO MAY 12, 1988



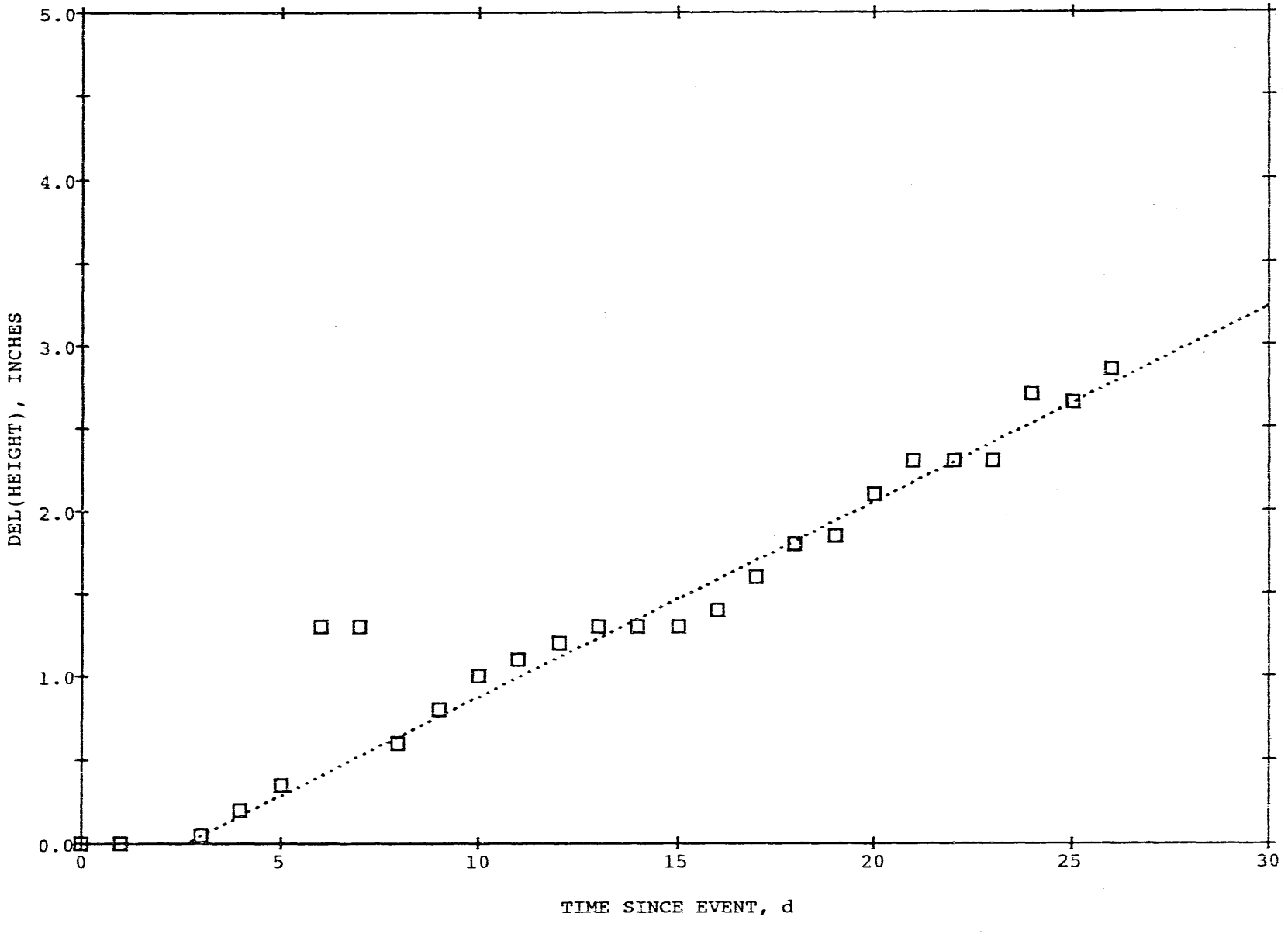
DETERMINATION OF KINETIC PARAMETERS FORGAS BUILD UP IN TANK 241-SY-101 FROM APRIL 27, 1990 TO JULY 23, 1990



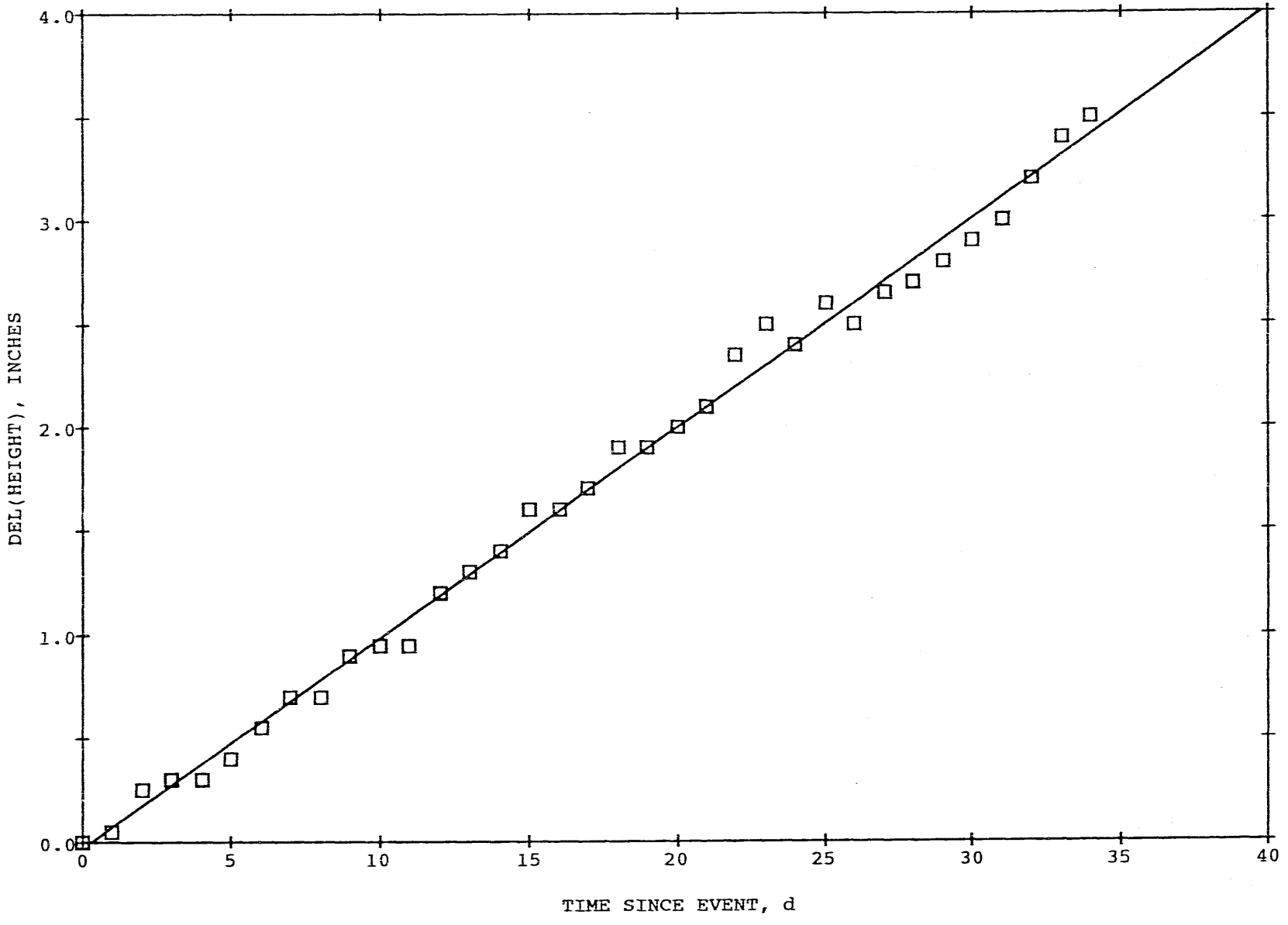
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
IN TANK 241-SY-101 FROM JANUARY 21 TO MARCH 14, 1981



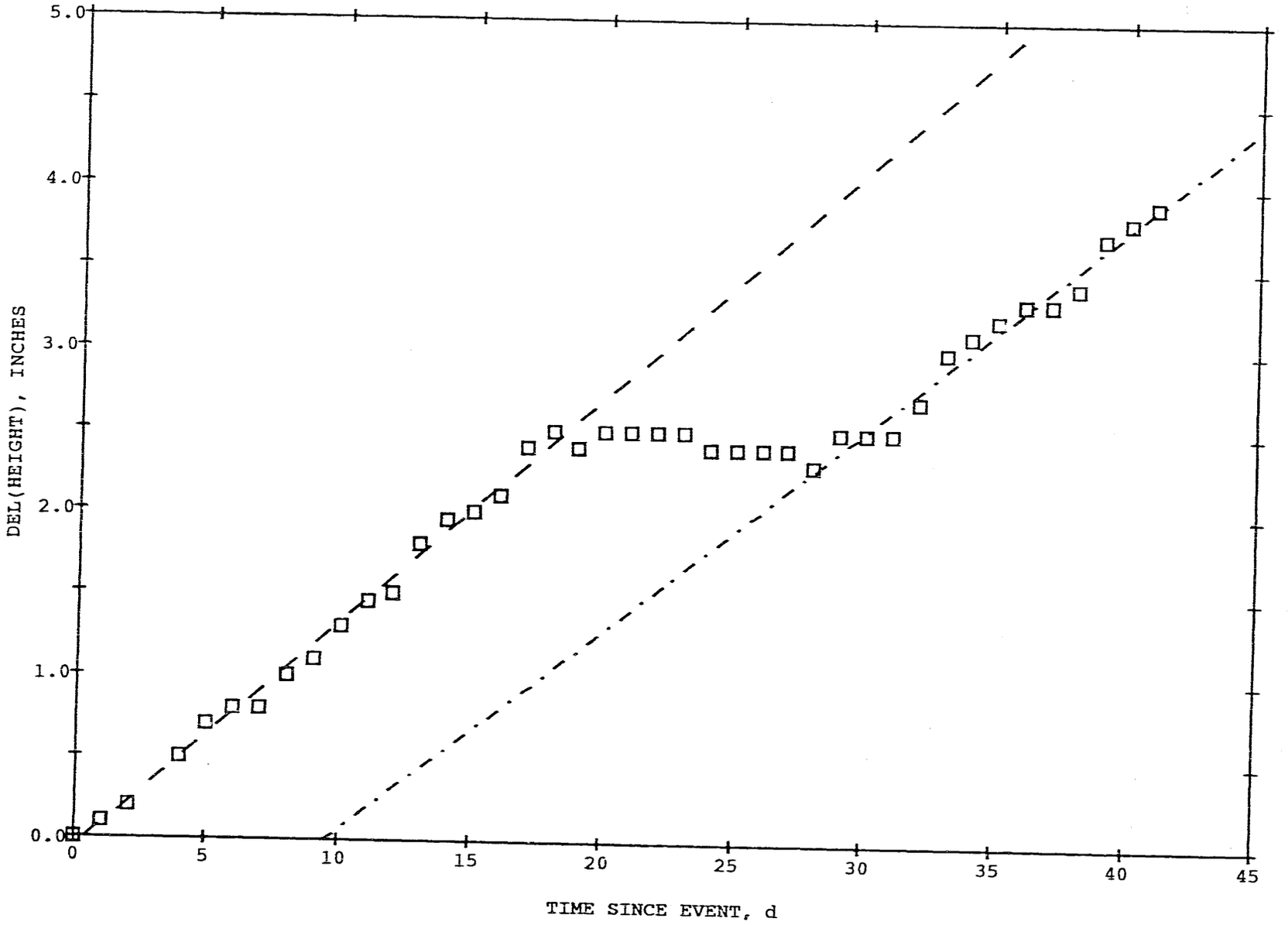
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
IN TANK 241-SY-101 FROM MARCH 5, 1982 TO MARCH 31, 1982



DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
IN TANK 241-SY-101 FROM MARCH 15, 1983 TO APRIL 18, 1983



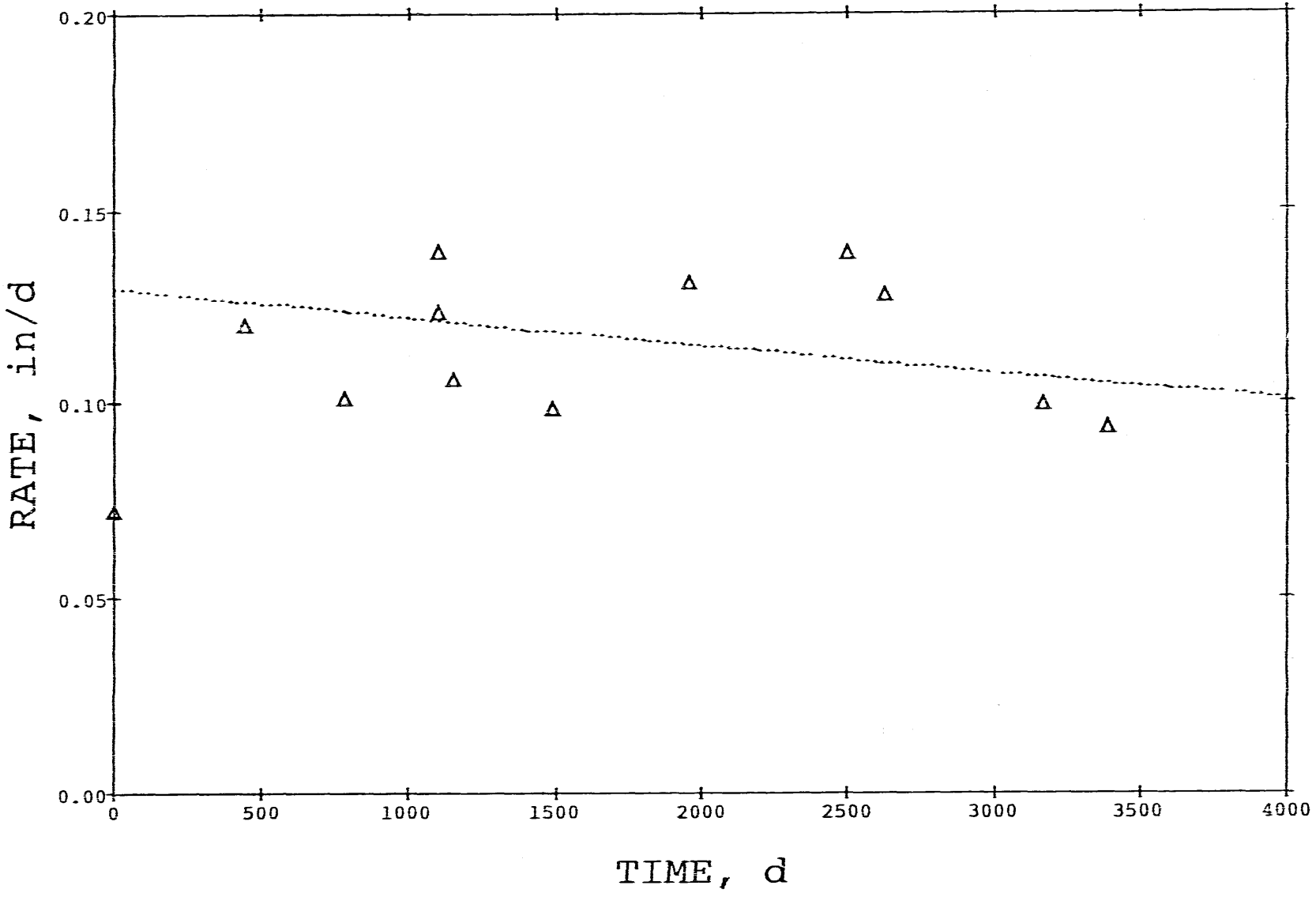
DETERMINATION OF KINETIC PARAMETERS FOR GAS BUILD UP
IN TANK 241-SY-101 FROM JANUARY 26, 1984 TO MARCH 7, 1984

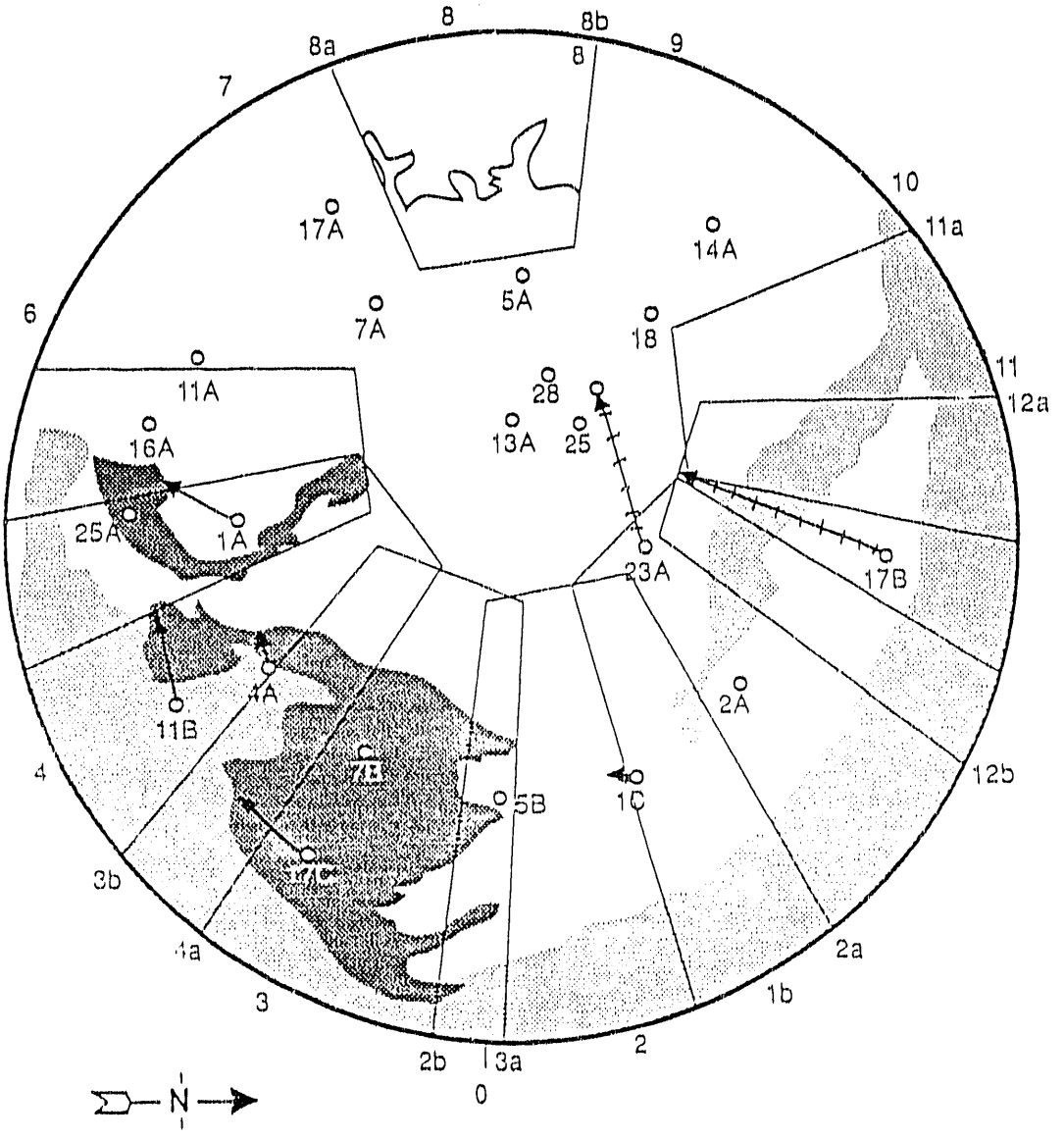


CONCLUSIONS FROM TANK HEIGHT DATA

- RATE IS INDEPENDENT OF TIME FOR SHORT TIMES
- RATE IS INDEPENDENT OF THE PHYSICAL EVENTS
- RATE IS INDEPENDENT OF TEMPERATURE OVER THE TEMPERATURES OF THE TANK
- RATE IS INDEPENDENT OF H_2 AND N_2O PRESSURES
- RATE IS CONSISTENT WITH ^{137}Cs OR ^{90}Sr DECAY

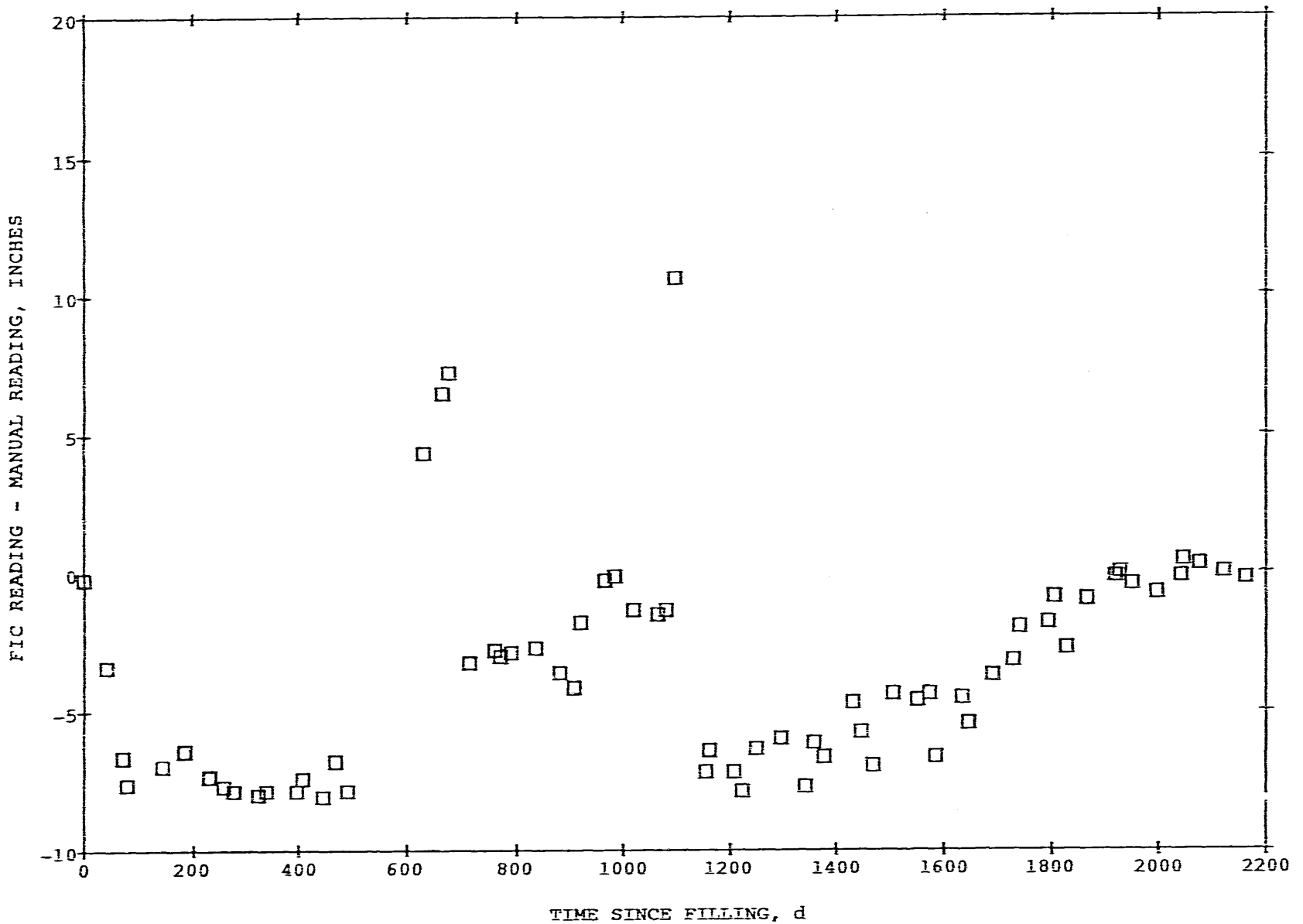
COMPARISON OF THE RATE OF GAS PRODUCTION WITH CESIUM DE
FOR TANK 241-SY-101 FROM MARCH 13, 1984 TO DECEMBER 19



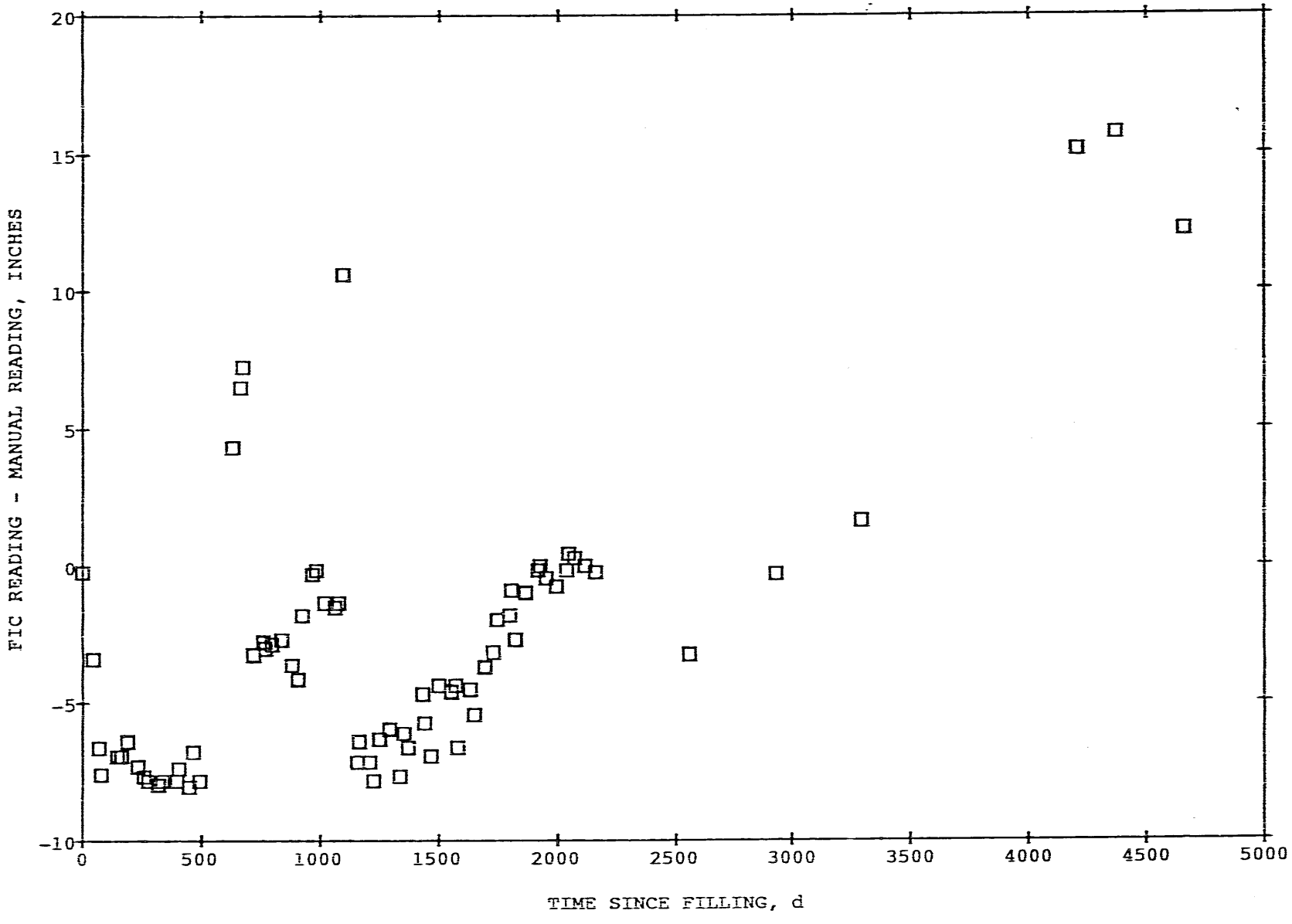

8
8b
8a
8
9
7
10
11a
17A
14A
5A
6
7A
18
11
11A
28
12a
16A
13A
25
25A
1A
23A
17B
4A
2A
11B
4
12b
5B
1C
3b
4a
2a
3
1b
2
2b
3a
0
N

R9102038.1

COMPARISON OF THE FIC READING AND THE MANUAL TAPE READING
FROM TANK 241-SY-101 INDICATING CRUST GROWTH



COMPARISON OF THE FIC READING AND THE MANUAL TAPE READING
FROM TANK 241-SY-101 INDICATING CRUST GROWTH



CONCLUSIONS FROM HEIGHT DIFFERENCE DATA

- CRUST MAY HAVE FORMED EARLY IN TANK HISTORY
- CRUST IS PARTIALLY FORMED BY EJECTION OF WASTE FROM UNDER THE CRUST
- OLD CRUST IS THINNER, DRIER, AND HIGHER IN CARBONATE CONTENT
- GAS RELEASE IS PROBABLY A COMBINATION OF FLOW THROUGH CRUST FISSURES AND POROUS MEDIA
- CRUST MODEL IS CONSISTENT WITH HEIGHT MEASUREMENTS, GAMMA SCANS, AND PICTURES

FUTURE WORK

- STATISTICAL TREATMENT OF THE RATES
- COMPARISON OF DATA WITH DATA FROM OTHER TANKS
- OBTAIN ADDITIONAL DATA FROM DAN REYNOLDS

ATTACHMENT D

DXRD STUDIES OF SYNTHETIC CRUST REACTIONS

CRUST PREPARED AT WESTINGHOUSE (Herting)

DSC and TGA EXPTS IN AIR AND N_2

DXRD:

- IN-SITU XRD with DYNAMIC DATA ACQUISITION
- TEMPERATURE PROGRAMMING
- CONTROLLED GAS ATMOSPHERE
- ON-LINE GAS ANALYSIS (NO_x, CO_2)

FIGURE 2 - SYN. CRUST AT 90°C (N_2)

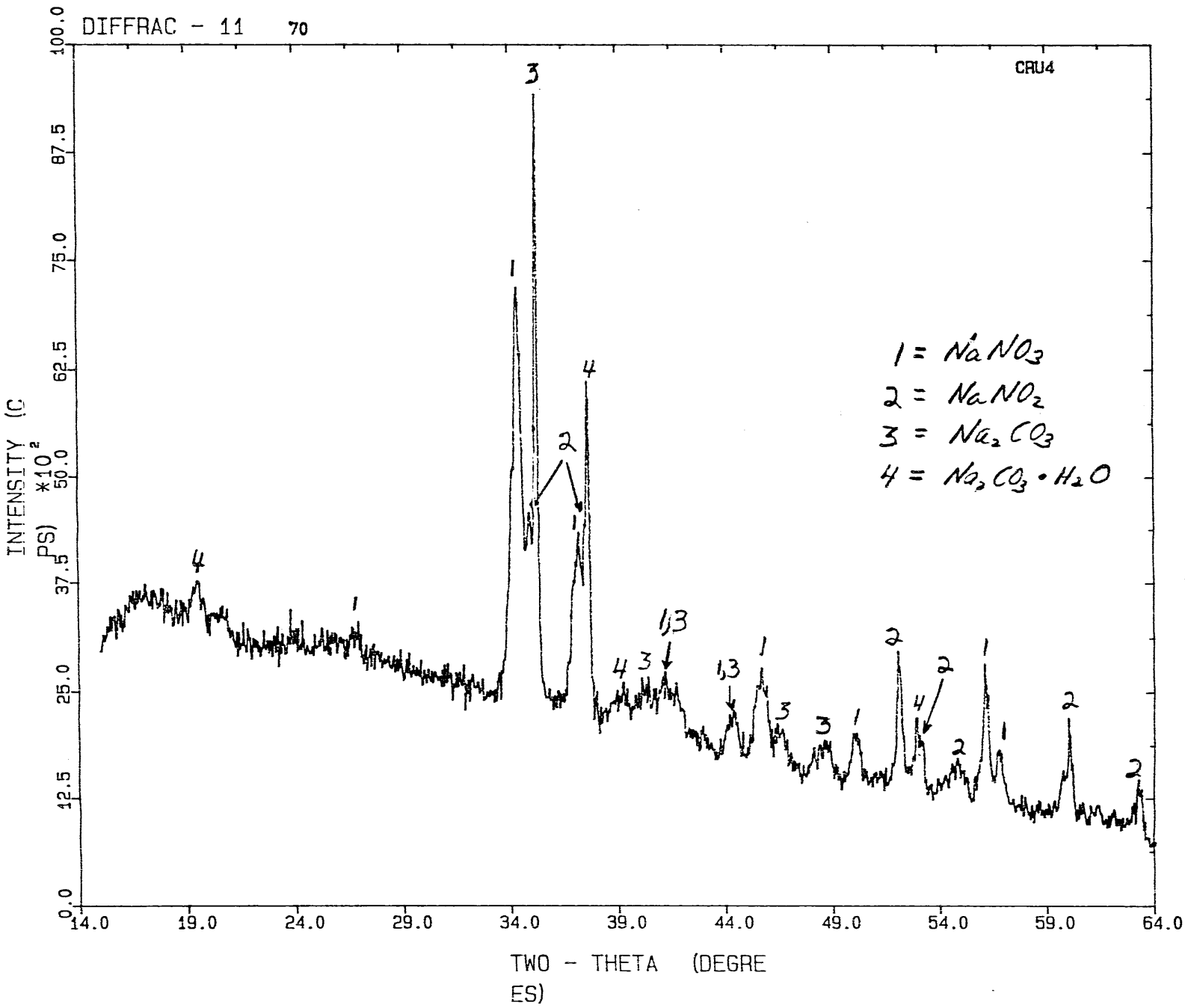


FIGURE 3
(5 °/MIN IN N_2)

HANFORD CRUST MATERIAL

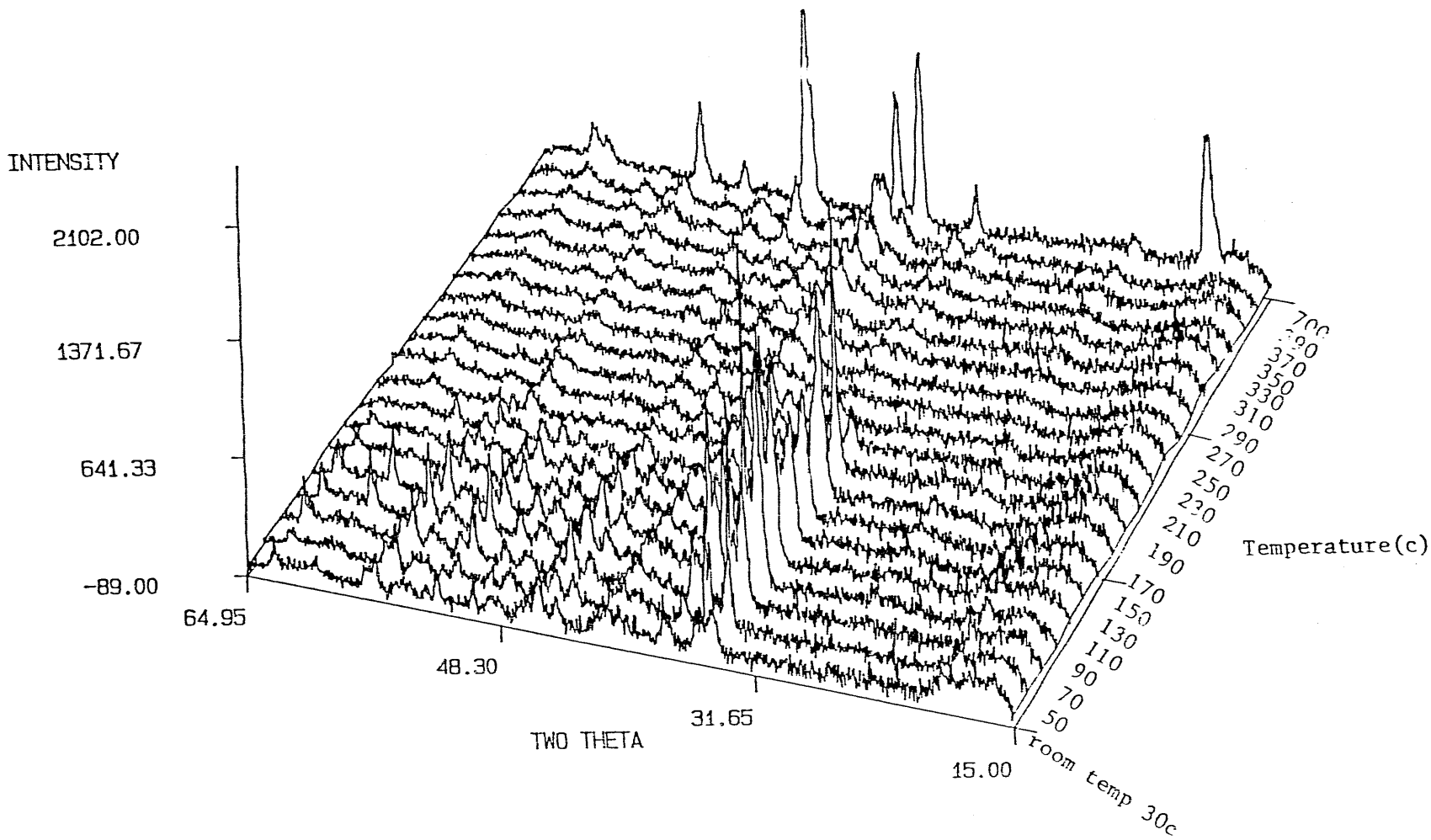


FIGURE 5
(5 °/MIN IN N_2)

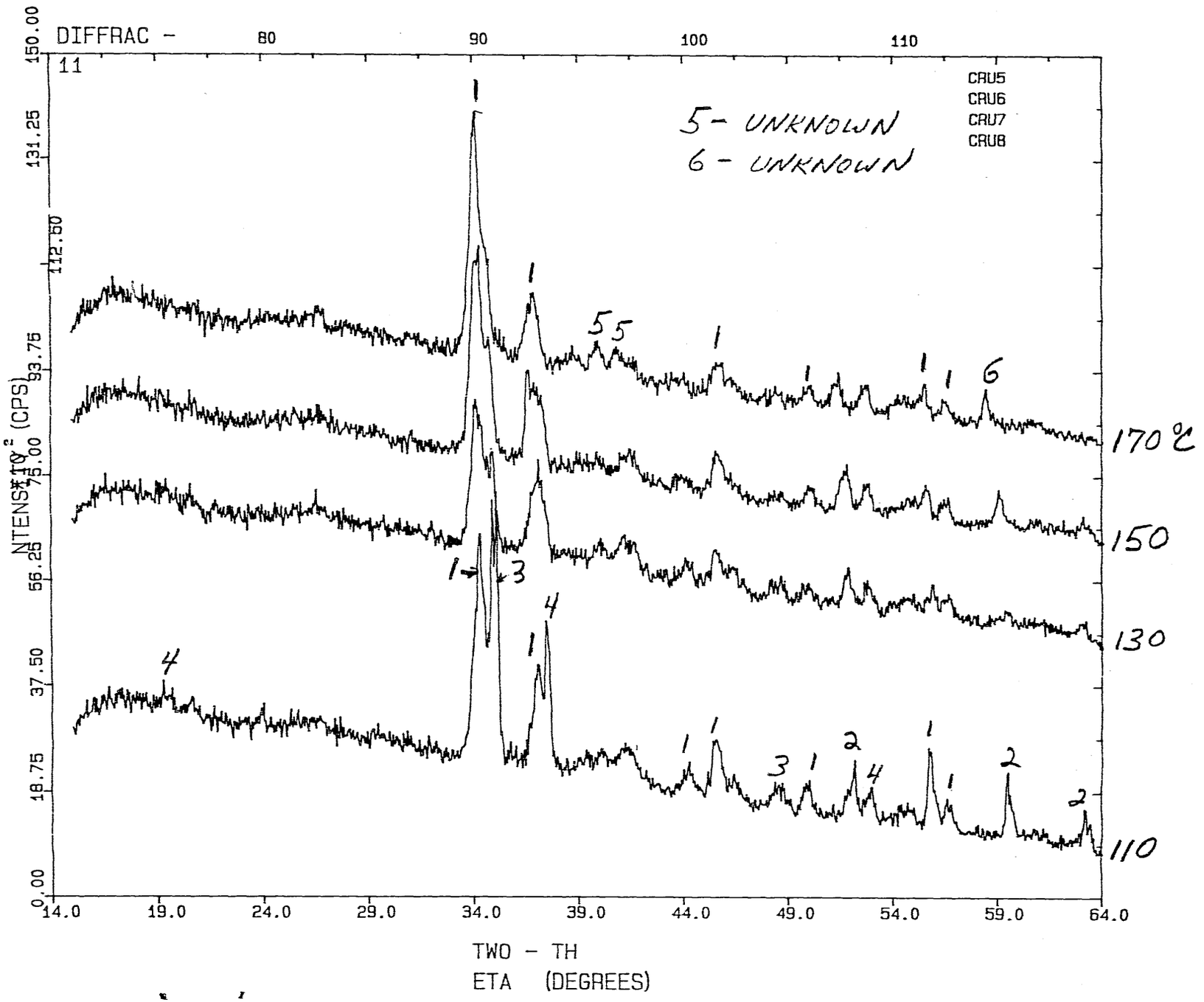
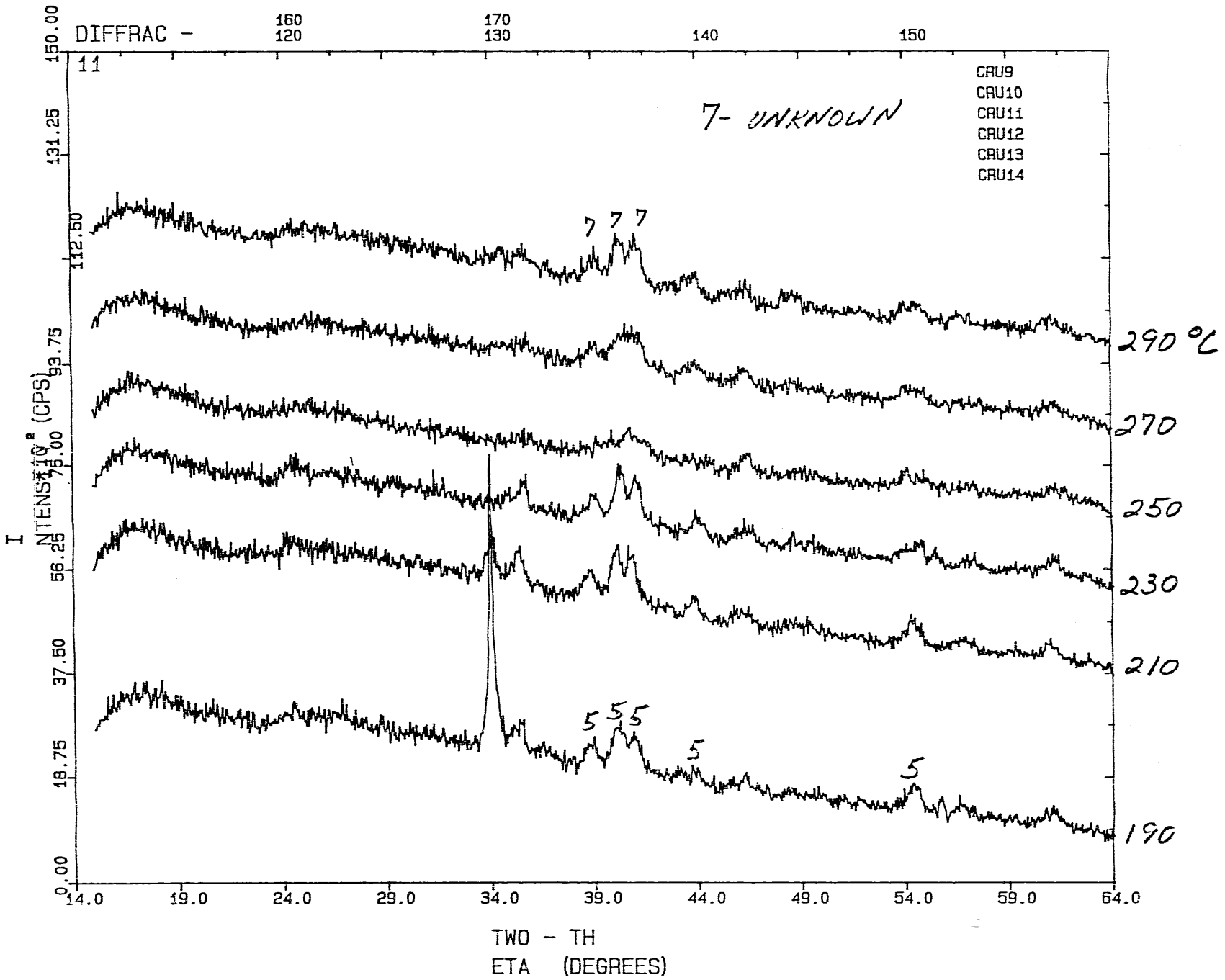
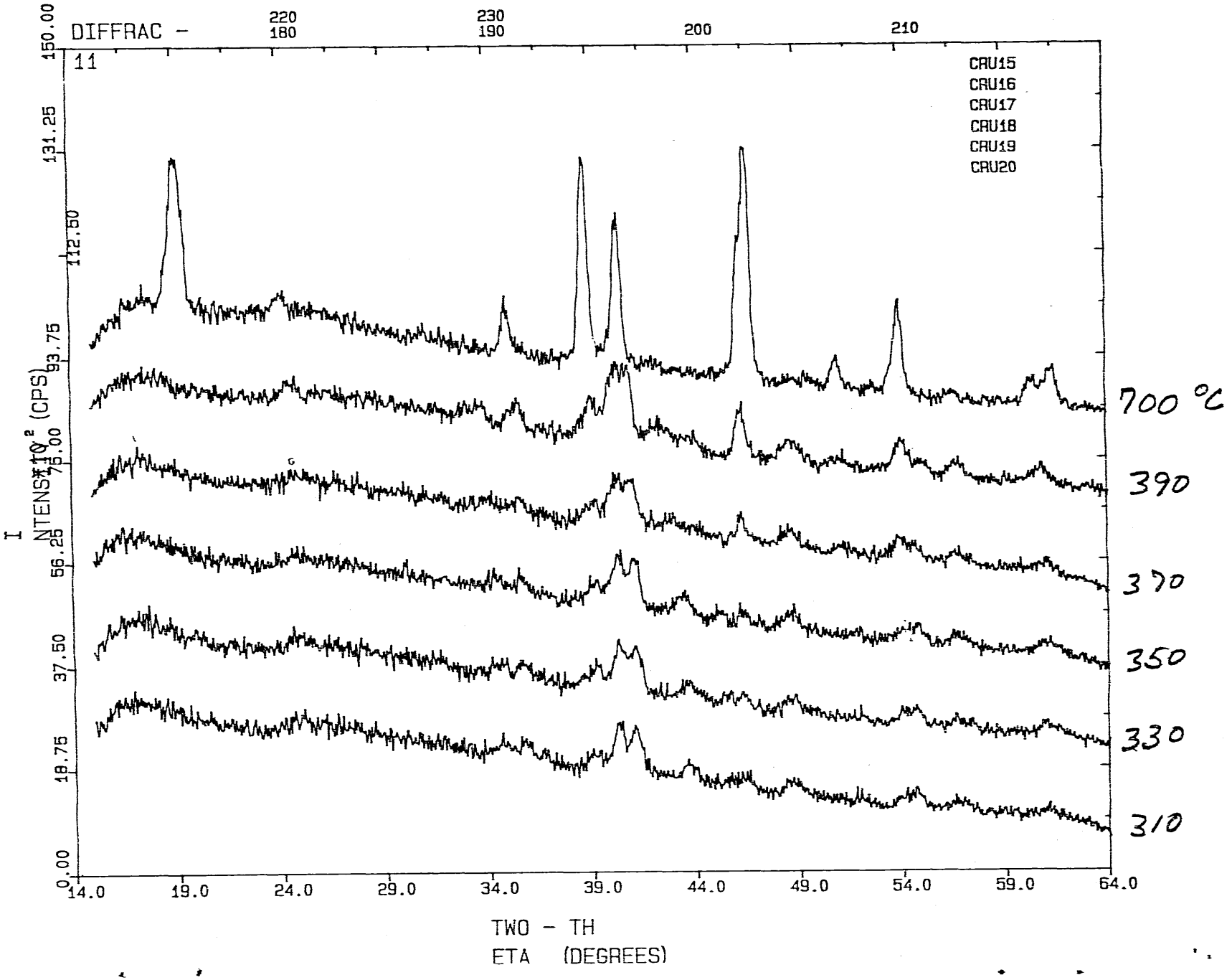


FIGURE 6
(5°/MIN IN N_2)



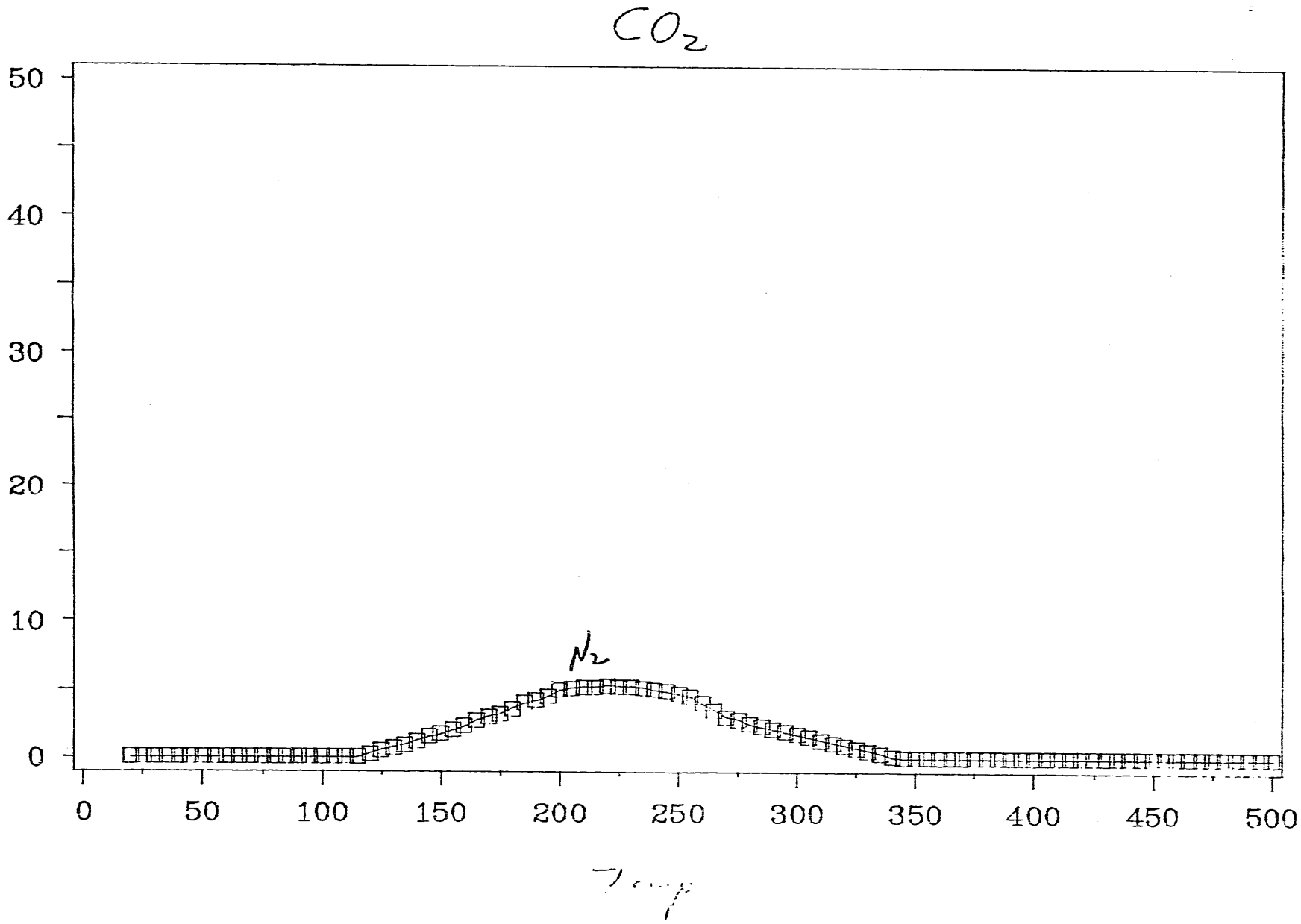
D.5

FIGURE 7
(5 °/MIN IN N_2)

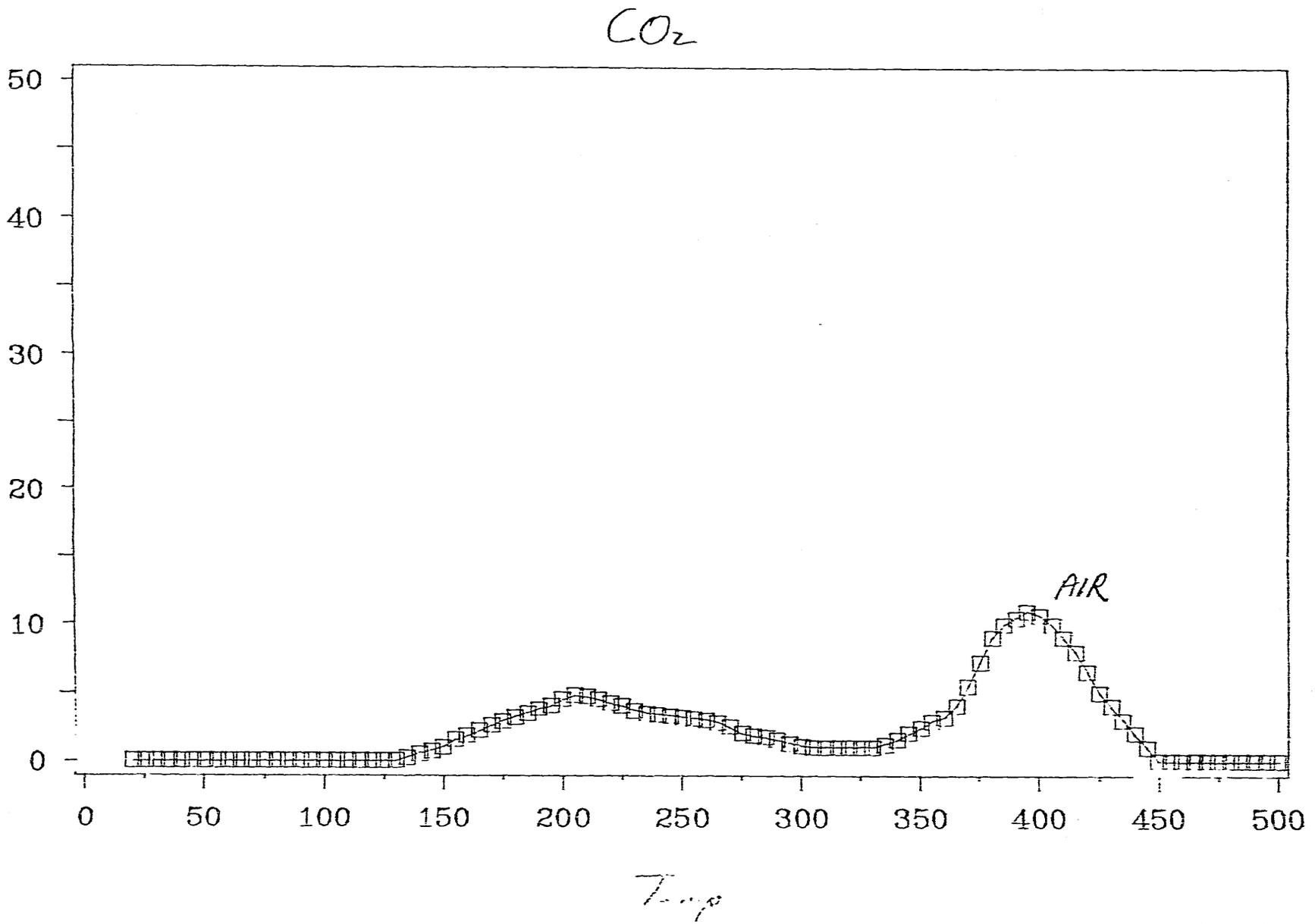


D.6

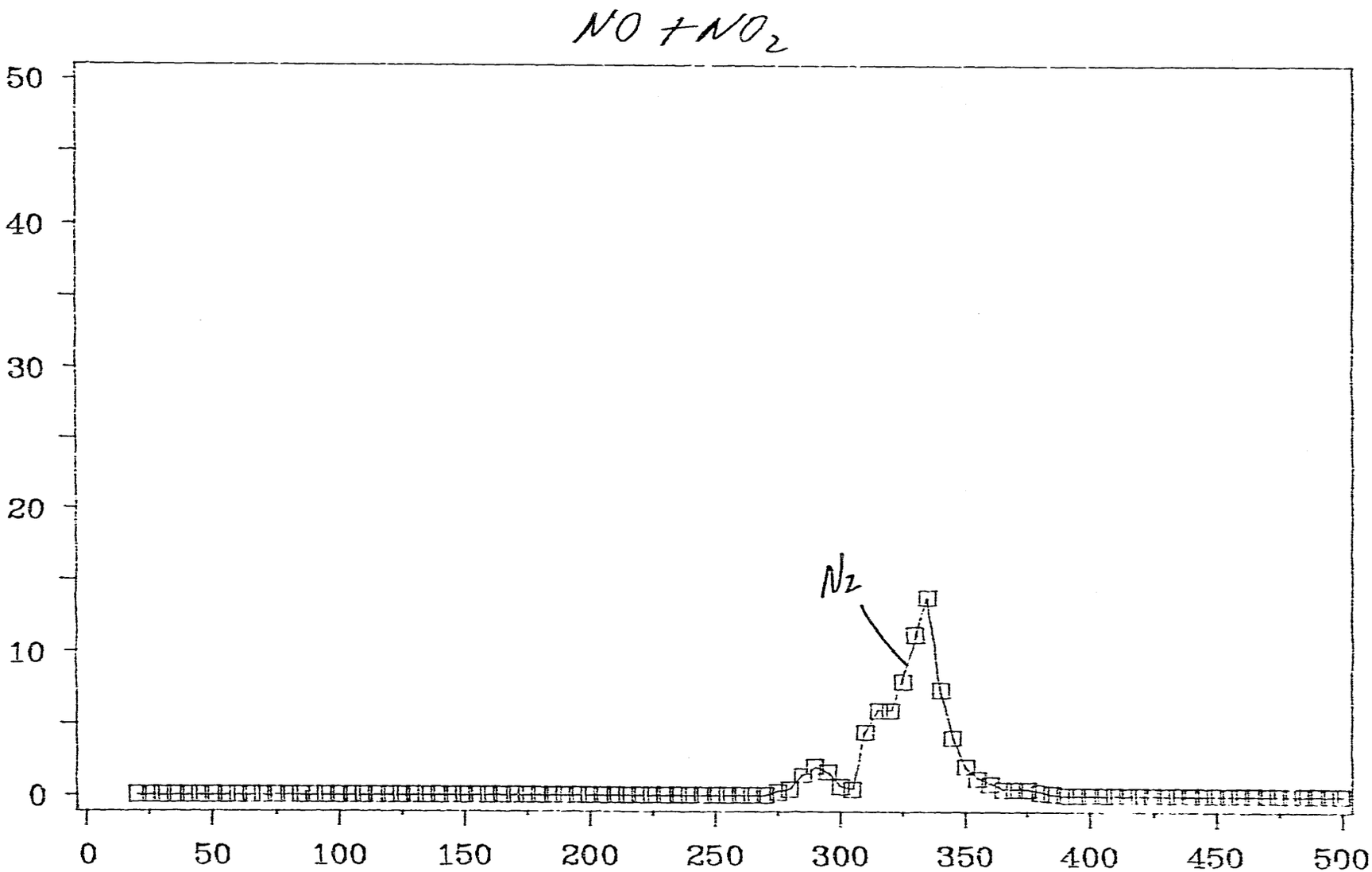
[illegible]
CO_2 emission
Heated in Nitrogen
5 deg / min



CO_2 Emission
Heated in Air
5 deg / min

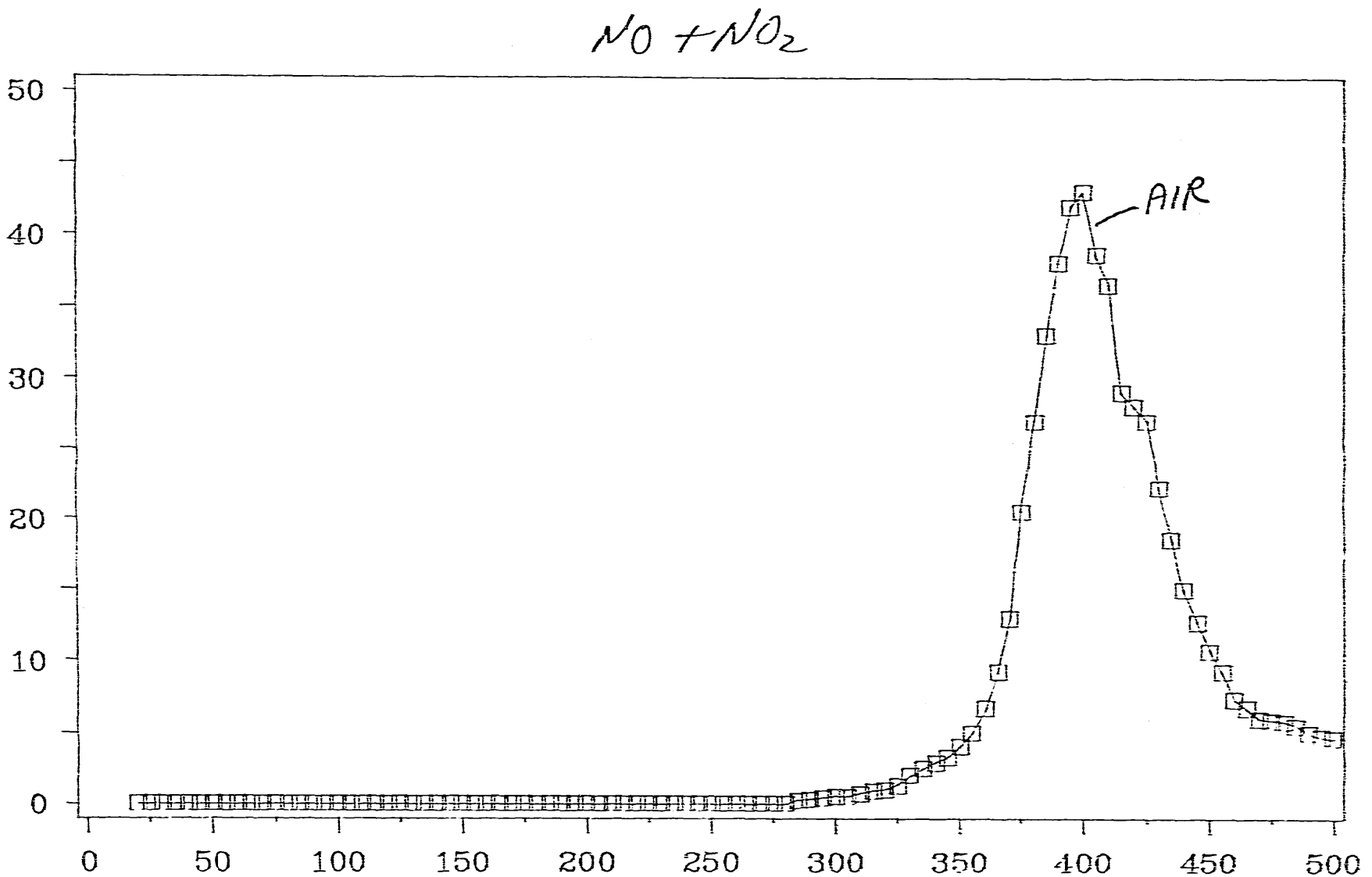


NO_2 Emission
Heated in Nitrogen
5 deg / min



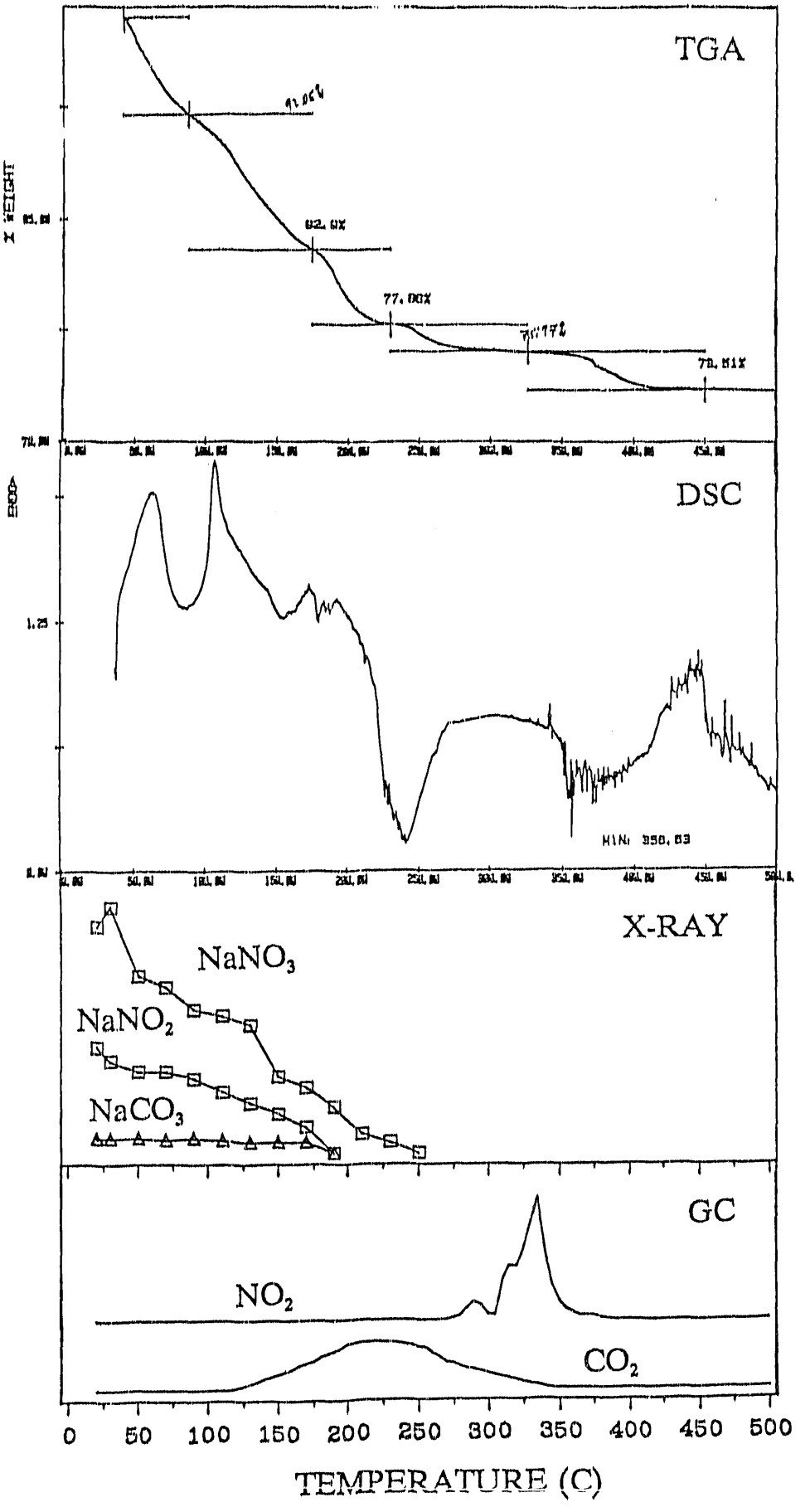
D.9

NiZ Emission
Heated in Air
5 deg/min

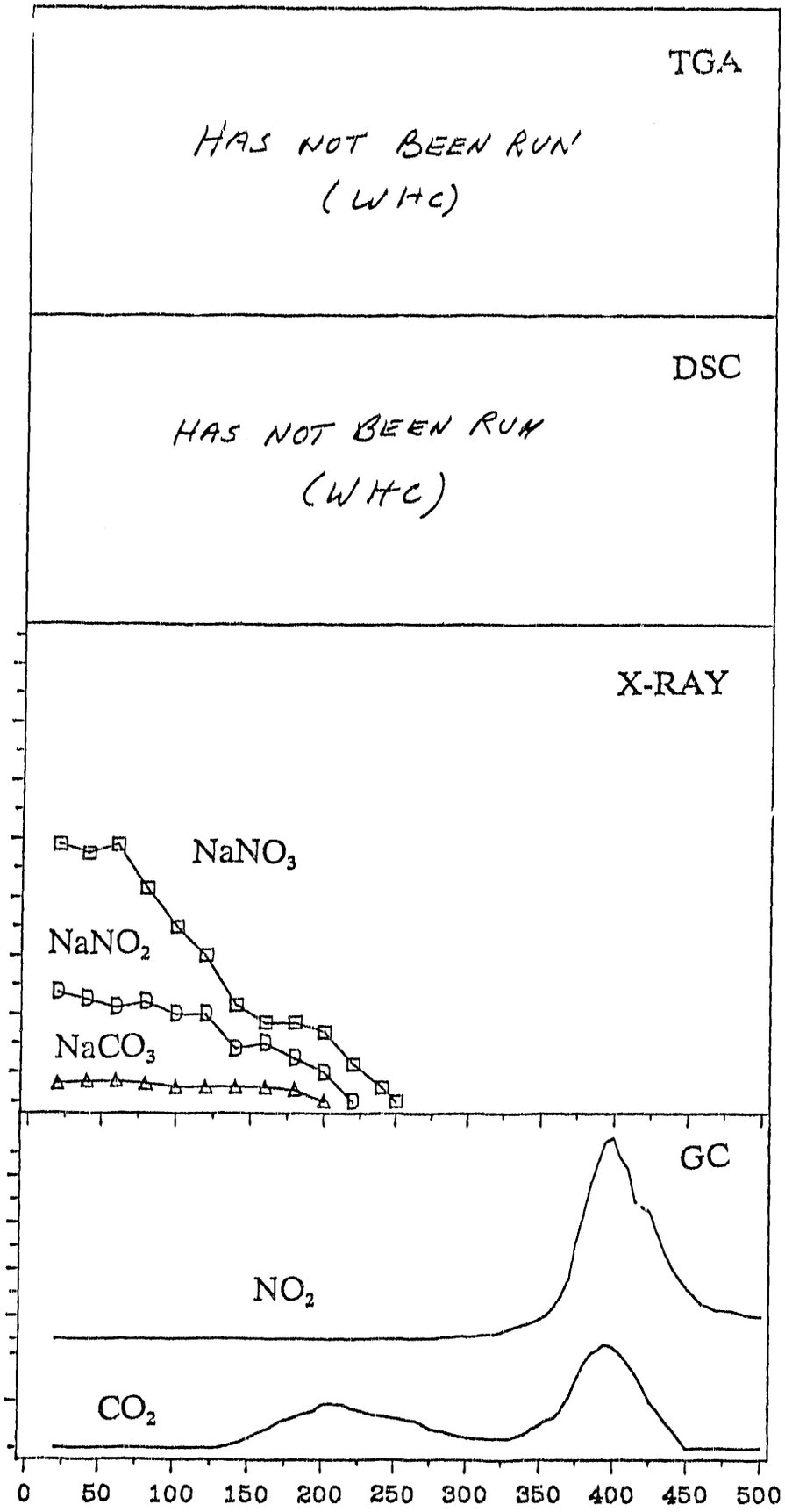


D.10

SYN CRUST (IN N_2, 5 deg min)



SYN CRUST (IN AIR, 5 deg min)



TEMPERATURE (C)

ATTACHMENT E

Westinghouse Hanford Company

Internal Memo

From: Process Chemistry Laboratories 28110-PCL91-009
Phone: 3-2532 T6-50
Date: January 29, 1991
Subject: TANK 101-SY CRUST SAMPLES, ANALYTICAL RESULTS, FINAL REPORT

To: J. L. Deichman B3-86

cc: Distribution
D. B. Bechtold DBB
DLH File/LB
Process Aids (Tank Farms)

References:

(1) Memo, J. R. Jewett and H. Babad to J. L. Deichman, "Preliminary Total Organic Carbon Analysis TK-101-SY Crust Samples", dated December 4, 1990.

(2) Memo, J. R. Jewett and H. Babad to J. L. Deichman, "Preliminary Radionuclide Analysis TK-101-SY Crust Samples", dated December 21, 1990.

(3) Memo, J. R. Jewett and H. Babad, "Preliminary Chemical Analysis of TK-101-SY Crust Samples", dated January 4, 1991.

(4) Memo, D. L. Herting to G. D. Johnson, "Tank 101-SY Crust Sample Recovery and Visual Observations", dated December 7, 1990.

(5) Memo, B. M. Mauss to L. M. Sasaki, "101-SY Samples: Laboratory Analysis and Results", dated May 30, 1986.

(6) Memo, J. R. Jewett and H. Babad to J. L. Deichman, "Preliminary Thermal Analysis TK-101-SY Crust Samples", dated November 29, 1990.

(7) Memo, D. B. Bechtold to J. L. Deichman, "Thermal Analysis of 101-SY Crust Samples", dated December 31, 1990.

Three crust samples were removed from Tank 101-SY on Sunday, November 18, 1990. The samples were taken by removing three level detectors from the tank: the sludge weight, the manual tape plummet, and the Food Instrument Company (FIC) plummet. This memo describes the chemical and radionuclide analytical results for the crust samples. It supercedes the preliminary analytical results reported in references 1-3. Analytical summaries are presented in tables 1-4.

Details regarding recovery of the samples from their shipping containers can be found in reference 4. The total amounts of sample recovered were:

Manual Tape Plummet: 0.70 grams of very dry, chunky, dark gray solids.

FIC Plummet: 0.27 grams of very dry, powdery, yellow solids.

Material recovered from the sludge weight (SW) was divided into three fractions based on appearance and origin:

SW/Wet: 67 grams of very dark brown, moist, sticky solids the consistency of peanut butter, taken from inside the "donut hole" of the sludge weight.

SW/Dry: 11 grams of very dark brown, dry, flaky solids, scraped off the outer surfaces of the sludge weight.

SW/Loose: 4.8 grams of dark brown, dry, chunky solids, recovered from the inside of the sludge weight retrieval device.

In general, all five samples (Manual Tape Plummet, FIC Plummet, SW/Wet, SW/Dry, and SW/Loose) were remarkably similar to one another in chemical composition (see table 1). They were also very similar to slurry samples taken from the tank in 1986 (reference 5). The major components in all the samples were sodium salts of nitrate, nitrite, carbonate, aluminate, and organic complexants. Details on the sample preparation, analytical determinations, and results follow.

DIRECT SAMPLE ANALYSES

Thermal analyses were done by the Process Chemistry Laboratories (PCL) on all the samples. These are reported in references 6 and 7. Weight percent water values determined by thermal analysis are included in tables 1 and 2 in this memo.

Because the sludge weight samples, in particular, were exposed for up to six hours to a significant air flow in the hot cell, an experiment was done using synthetic waste to determine how much moisture might have been lost during the recovery of the sludge weight samples.

Four sythetic crust samples were placed in open beakers or vials and exposed to air flow by placing them in a fume hood for six hours. The weight percent moisture was determined before and after the six hour period by measuring weight loss at 180°C. The air exposure resulted in a decrease in the average percent moisture from 25.5 percent to 20.5 percent. These results confirm that the percent moisture results reported in references 6 and 7 are conservative. The experimental conditions are sufficiently different between the sludge weight samples and the synthetics that a direct extrapolation should not be made.

After the thermal analyses were completed on the Manual Tape and FIC samples, the entire remaining samples were delivered to Analytical Laboratories (AL). A non-destructive gamma energy analysis (GEA) was run on each solid sample to give a qualitative indication of which radionuclides were present. A solid GEA gives only qualitative results because of the non-standard sample geometry. Results showed that Cs-137 was the major isotope found in both samples, and Eu-154 was identified in the manual tape sample only. No other gamma emitters were found. Solid GEA's were not done on the SW samples because there was sufficient sample to do quantitative GEA's on fusion-dissolved samples.

After AL had used virtually all of the Manual Tape and FIC samples to perform water digest analyses (see next section of report), the "empty" original sample containers were returned to PCL. Enough material was recovered to perform a limited examination with the polarized light microscope. Despite the large differences in physical appearance of the two samples, they looked very much alike under the microscope. Major crystalline phases that were identified based on crystal morphology and optical properties (mainly birefringence) were sodium nitrate and sodium carbonate. Other crystalline phases were suspected but could not be confirmed with the very limited amount of sample.

In the case of the three SW samples, individual subsamples were delivered to PCL for thermal analyses and to AL for chemical and radionuclide analyses. The remainder of each sample was archived. A portion of each archived sample will be sent to Pacific Northwest Laboratories (PNL) for total organic carbon analysis as soon as a work order is in place to fund the PNL work.

Polarized light microscopy for the SW samples was performed by PCL on the unused portions of the thermal analysis subsamples. All three samples looked very similar to the Manual Tape and FIC samples. Crystalline phases that were positively identified were sodium nitrate, nitrite, carbonate, aluminate, phosphate, and either chloride or fluoride. The samples also contained some unidentified crystalline and non-crystalline phases.

X-ray diffraction analyses were performed by AL on the three SW samples. Results were the same for all three, with the only crystalline phases identified being sodium nitrate and nitrite.

WATER DIGEST

A water digest was performed by AL on all five samples. Larger-than-normal dilution factors were necessary for the Manual Tape and FIC samples because of the limited amount of sample available. These large dilution factors led to correspondingly large uncertainties in the analytical results, especially for the FIC sample, which had the largest dilution factor.

Analyses performed on the leachates from the water digest were: total water-soluble organic carbon (TOC), carbonate, hydroxide (or pH), and Dionex ion chromatography (for nitrate, nitrite, fluoride, chloride, phosphate, and sulfate). In addition, GEA and inductively coupled plasma (ICP) analysis for metal ion concentrations were performed on the water leachates from the Manual Tape and FIC samples. Normally, the ICP analysis is done on an acid leachate, and the GEA is done on the fused/dissolved sample, but there was no more sample available for these two samples to perform an acid digest or fusion. For the sake of comparison, GEA was also performed on the water leachate for the three SW samples.

All of the organic compounds that are known to be present in Tank 101-SY are at least moderately water soluble. These include sodium salts of the common complexing agents and their degradation products, all of which are water soluble by virtue of their highly polar amine and hydroxy functional groups and/or their negatively charged carboxylate functional groups. In order to account for the possibility that the crust samples might contain non-polar (water insoluble) organic compounds, portions of the SW samples are being sent to PNL, where a true total organic carbon analysis will be run directly on the solid samples.

Chemical analysis results are shown in tables 1-3. GEA results are shown in table 4 along with other radionuclide results. For a full discussion of the results shown in the tables, see the approriate section later in this memo.

The preliminary report on total organic carbon analysis (reference 1) contained an error in the table where weight percent TOC and sodium carbonate were reported. The SW/DRY and SW/WET labels were interchanged in the table. The values reported in this memo have been corrected.

SIMULANT ANALYSIS

As an independent check on AL water leach and analysis procedures, two simulated crust samples were prepared and submitted to AL for analysis soon after the actual samples were submitted. The simulants were designed to test: (1) whether TOC is reported when none is actually present, (2) how accurate the reported TOC value is compared to a known value which is close to the amount reported for the actual samples, (3) whether the presence of Na_4EDTA has any effect on the reported value for nitrate, and (4) indirectly, how complete the water digestion is.

Both simulants contained about equal amounts of dry, powdered $NaNO_3$, $Mg(OH)_2$, and Na_2CO_3. One of the simulants also contained an amount of $Na_4EDTA \cdot 2H_2O$ to equal 2.6 percent TOC. As the following table shows, analytical results ("found") were very close to the known values ("actual"):

	SYSIM-1		SYSIM-2	
	Actual	Found	Actual	Found
wt% TOC:	0.00	0.13	2.64	2.99
wt% Na_2CO_3:	31.6	31.1	30.1	29.9
wt% $NaNO_3$:	34.5	35.4	29.7	29.9

ACID DIGEST

An acid digest was performed only on the three SW samples. Acid leachates were analyzed by ICP for metal ion concentrations, which are shown in table 2.

FUSION

Water leach and acid leach normally result in incomplete sample dissolution. In order to accomplish complete dissolution, samples are fused with molten potassium hydroxide, then dissolved in hydrochloric acid. Radionuclide analyses are performed on the fused/dissolved solution. Cation analyses by ICP are not done on fused samples because of the huge amount of potassium introduced by the fusion. Anion analyses are not done because of the large dilution factors accompanying fusion.

Results of the radioanalyses, which are unchanged from the preliminary report (reference 2) except for Np-237, are shown in table 4. A review of the preliminary report by Waste Tank Safety Analysis indicated that the "less than" values reported for Np-237 were too high to be useful. The neptunium extraction procedure was repeated for the sludge weight samples, but using the acid leachate instead of the fusion sample. Because of the smaller dilution factor, the dectection limit is lower. The difficulty here is the assumption that all of the neptunium dissolves in the acid digestion. While this is a reasonable assumption, it cannot be proved. Both fusion and acid leach results for Np-237 are given in table 4.

Included in the table for comparison are the radiochemical analyses of the "Middle" slurry sample taken from Tank 101-SY in 1986, and reported in reference 5. This was a dip sample taken from approximately the middle of the waste slurry, below the crust, and reported to be a "murky, brownish-gray slurry" containing twenty-eight volume percent filtered solids. The analyses shown in the table are for the slurry as a whole.

While there are some noticeable differences between the sludge weight analyses and the 1986 sample results, they are by-and-large well within the same range. The current samples (including the FIC and Manual Tape) are remarkably consistent from one sample to another in nearly all isotopes, especially

considering the large differences in the physical appearance of the samples. The Cs-137 values derived from sample fusion also agree well with those from water leach of the samples, showing that the cesium is water soluble. Cs-137 was the only gamma emitter identified by gamma energy analysis, except for the traces of Co-60 and Eu-154 found in the Manual Tape sample, as shown in table 4.

DISCUSSION OF TABLES 1-3

Table 1 gives the analytical results for all five samples on the basis of weight percent sodium salts, relative to the total weight of as-received sample. (As-received sample means the sample as-received by the people performing the analyses. As discussed earlier, the samples could be drier as-received than when the samples were removed from the tank.)

Values in table 1 are the same as those presented in the preliminary report (reference 3) except for the following changes:

> For the Manual Tape and FIC samples, the "zero" entries for Na_3PO_4 have been replaced by "less than" values. Column totals remain unchanged.
>
> For the SW/LOOSE sample, the Na_2SO_4 entry has been changed from 1 percent to 6 percent to correct a calculation error in the preliminary report. The column total has been changed from 92 percent to 97 percent.
>
> A typographical error in the last column heading has been corrected.

The data in table 1 have been rather heavily "massaged" to put them into an understandable format. The raw data (slightly massaged) are presented in table 2 to show how table 1 was calculated.

Weight percent values in table 1 were calculated from the analyzed concentration of each anion, assuming the associated cation is sodium. This assumption is supported by the ICP results (table 2), which showed that sodium represents 95-98 percent of the total cations present in the samples.

Sodium aluminate is expressed as $NaAlO_2$ rather than as $NaAl(OH)_4$ or as $NaAlO_2 \cdot 2H_2O$ because the water of hydration is included in the table as part of the "water" entry.

The "$NaOOCCH_3$" ertry is derived from the total organic carbon (TOC) by multiplying the TOC by the factor 3.4 to convert from grams of carbon to grams of sodium acetate. Sodium acetate was chosen because "acetate equivalent" is frequently used as a measure of total organic carbon, and because it has a total weight/carbon ratio (3.4) which is fairly typical of the organic compounds likely to be present. For comparison, the ratio for Na_4EDTA is 3.2.

The "metals" entry is the total weight of all metals found in the sample other than sodium and aluminum. These include Ca, Cr, Fe, Ni, K, and Si. No attempt was made to adjust the weights to account for the species that might actually be present in the samples (e. g., Fe_2O_3), because the total weight is relatively trivial.

The "water" entry is taken from the thermal analysis data reported in reference 7.

The "total" of each column should equal 100 percent if all the analyses are exactly correct and all chemical species present in the samples have been accounted for. Overall, the mass balance results are within the expected error range for all samples except the FIC sample. The FIC results reflect the large dilution factor necessitated by the inadequate amount of sample.

The mass balance results (i.e., column totals) shown in table 2 are actually a better representation of the validity of the data than the column totals in table 1, because table 2 contains relatively unmassaged data. In particular, the total amount of sodium accounted for in table 1 is arrived at by assumption (that there is enough sodium to balance the anions). The total amount of sodium accounted for in table 2 represents actual analytical results.

Another measure of the accuracy of the analytical results is the ratio of the total equivalents of anions to cations, shown in table 3. This ratio is very close to unity for all samples except the FIC sample, where the ratio of anions/cations is close to two. Since the cation total is so consistent from sample to sample, the anion results appear to be more suspect for the FIC sample.

Calculation of the millimoles of each ion in table 3 is straightforward, as is the calculation of the total milliequivalents of cations and most anions. To calculate the total milliquivalents of organic anions, the total moles of carbon was multiplied by the factor 0.3. This factor was chosen as a representative number of negative charges per carbon atom for typical complexant molecules. For example, HEDTA has ten carbon atoms and three negative charges.

INTERPRETATION OF CHEMICAL ANALYSIS RESULTS

Analytical results for the major components are remarkably consistent from sample to sample, especially considering the large differences in physical appearance of the samples (reference 4). The preliminary chemical analysis is consistent with the limited exothermic activity found by thermal analysis (reference 7).

Results are also very consistent with the 1986 Middle Slurry sample. The major differences between the crust samples and the 1986 sample are in the carbonate, which is much higher in the crust samples, and the hydroxide, which

is much lower in the crust samples. These results confirm predictions based on exposure of a caustic solution over time to air containing carbon dioxide.

The only other major difference of note is the sulfate concentration, which was anomalously high in the Manual Tape sample and especially the FIC sample. The poor mass balance and ionic charge balance cast some doubt on the validity of the anion analyses for these two samples. However, in a qualitative sense, it is probably safe to say that the Manual Tape and FIC samples did contain relatively more sulfate than the Sludge Weight samples.

Please call if there are any questions or comments about how the data were derived or interpreted.

Dan Herting

D. L. Herting, Scientist
Process Chemistry Laboratories

tth

attachments: 4

TABLE 1

OVERALL COMPOSITION OF CRUST SAMPLES

WEIGHT%	SLUDGE WEIGHT SW/DRY	SW/WET	SW/LOOSE	MAN TAPE PLUMMET	FIC PLUMMET	MIDDLE SLURRY (REF 5)
$NaNO_3$	22	19	24	23	26	20
$NaNO_2$	18	13	17	14	25	16
$NaAlO_2$	12	12	13	11	3	13
Na_2CO_3	11	7	15	19	19	3
$NaOOCCH_3$	7	6	8	8	5	5
NaOH	3	5	0	1	1	8
NaCl	2	1	2	2	2	2
Na_3PO_4	2	2	2	<2	<9	2
Na_2SO_4	1	1	6	21	60	<1
Metals	2	1	1	1	1	1
Water	15	26	10	10	10	33
TOTAL	94	92	97	109	153	104

TABLE 2. RESULTS OF CHEMICAL ANALYSIS OF TANK 101-SY CRUST SAMPLES

(grams analyte per gram as-received solids)

	SW/DRY	SW/WET	SW/LOOSE	MAN TAPE	FIC
Water Leach:					
TOC	0.020	0.016	0.022	0.023	0.016
NO_3	0.158	0.138	0.178	0.167	0.193
NO_2	0.117	0.088	0.111	0.093	0.169
CO_3	0.064	0.039	0.087	0.105	0.110
Acetate	0.049	0.040	0.055	0.056	0.039
OH	0.014	0.019	0.001	0.005	0.002
PO_4	0.013	0.009	0.009	<0.011	<0.051
Cl	0.010	0.007	0.009	0.010	0.014
SO_4	0.007	0.008	0.044	0.143	0.405
Acid Leach:				#	#
Na	0.243	0.240	0.289	0.272	0.246
AlO_2	0.087	0.085	0.093	0.078	0.023
Cr	0.007	0.009	0.000	0.003	0.001
Fe	0.006	0.001	0.003	0.000	0.000
K	0.003	0.003	0.004	0.004	0.005
Si	5e-04	3e-04	2e-04	4e-04	0.002
Ca	4e-04	3e-04	5e-04	4e-04	4e-04
Ni	3e-04	3e-04	0	4e-04	0
From Reference 7:					
H_2O	0.150	0.260	0.100	0.100	0.100
TOTAL (*)	0.931	0.945	0.984	1.038	1.311

(*) - Total includes all weights except TOC, which is incorporated into the 'acetate' entry. Total should equal 1.000 (see text).

(#) - These ICP results taken from water digest sample, not acid digest.

TABLE 3. ANION:CATION BALANCE IN WATER SOLUBLE FRACTION					
	(mmoles per gram as-received solids)				
	SW/DRY	SW/WET	SW/LOOSE	MAN TAPE	FIC
ANIONS					
TOC, mmol/g	1.66	1.36	1.86	1.91	1.32
NO_3	2.55	2.23	2.87	2.70	3.11
NO_2	2.55	1.91	2.41	2.02	3.68
CO_3	1.07	0.65	1.45	1.75	1.84
OH	0.82	1.09	0.06	0.31	0.09
PO_4	0.13	0.09	0.09	0.00	0.00
Cl	0.28	0.19	0.27	0.28	0.40
SO_4	0.08	0.08	0.46	1.49	4.22
AlO_2	1.48	1.44	1.58	1.32	0.39
CATIONS:					
Na	10.56	10.43	12.57	11.81	10.70
K	0.09	0.07	0.09	0.11	0.14
TOT ANIONS, MEQ/G	10.87	9.01	11.85	13.69	20.19
TOT CATIONS, MEQ/G	10.64	10.50	12.66	11.92	10.84
ANION:CATION RATIO	1.02	0.86	0.94	1.15	1.86

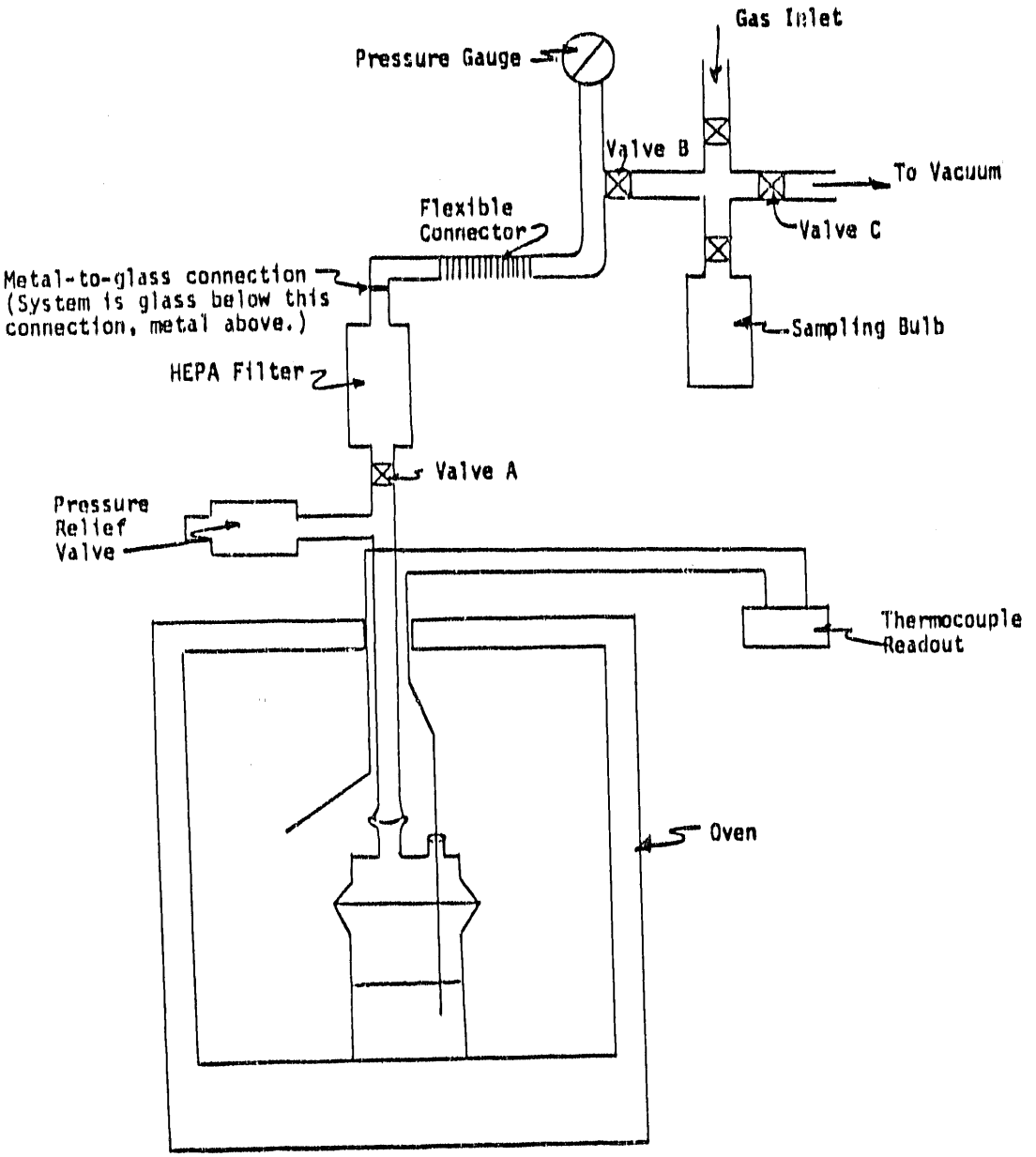
* TOT ANIONS = 0.3*TOC + NO_3 + NO_2 + 2*CO_3 + OH + 3*PO_4 + Cl + 2*SO_4 + AlO_2
* TOT CATIONS = Na + K
* MEQ/G = milliequivalents per gram as-received solids

TABLE 4

RADIONUCLIDE ANALYSIS RESULTS

		SLUDGE WEIGHT			MANUAL TAPE PLUMMET	FIC PLUMMET	MIDDLE SLURRY (REF. 6)
		SW/DRY	SW/WET	SW/LOOSE			
FUSION:							
Total beta	uCi/g*	560	427	661	INSUFFICIENT SAMPLE FOR FUSION		930
Total alpha	uCi/g	<0.08	<0.15	0.25			---
Cs-137	uCi/g	434	315	469			539
U (Total)	g U/g	0.00011	0.00011	0.00010			<1E-5
Pu-239/240	uCi/g	<0.0039	<0.0031	<0.0073			0.013
Am-241	uCi/g	0.010	<0.005	0.016			<0.012
Np-237	uCi/g	<0.56	<0.47	<0.62			---
Tc-99	uCi/g	0.48	0.40	0.43			0.15
I-129	uCi/g	<0.01	<0.008	0.012			---
Sr-90	uCi/g	13	23	98			5.6
WATER LEACH:							
Cs-137	uCi/g	477	328	417	492	501	---
Co-60	uCi/g	<0.22	<0.036	<0.053	0.098	<0.076	---
ACID LEACH							
Np-237	uCi/g	<0.07	<0.11	<0.10	---	---	---
GEA-SOLID:	---	---	---	---	Cs-137	Cs-137	---
	---	---	---	---	Eu-154	---	---

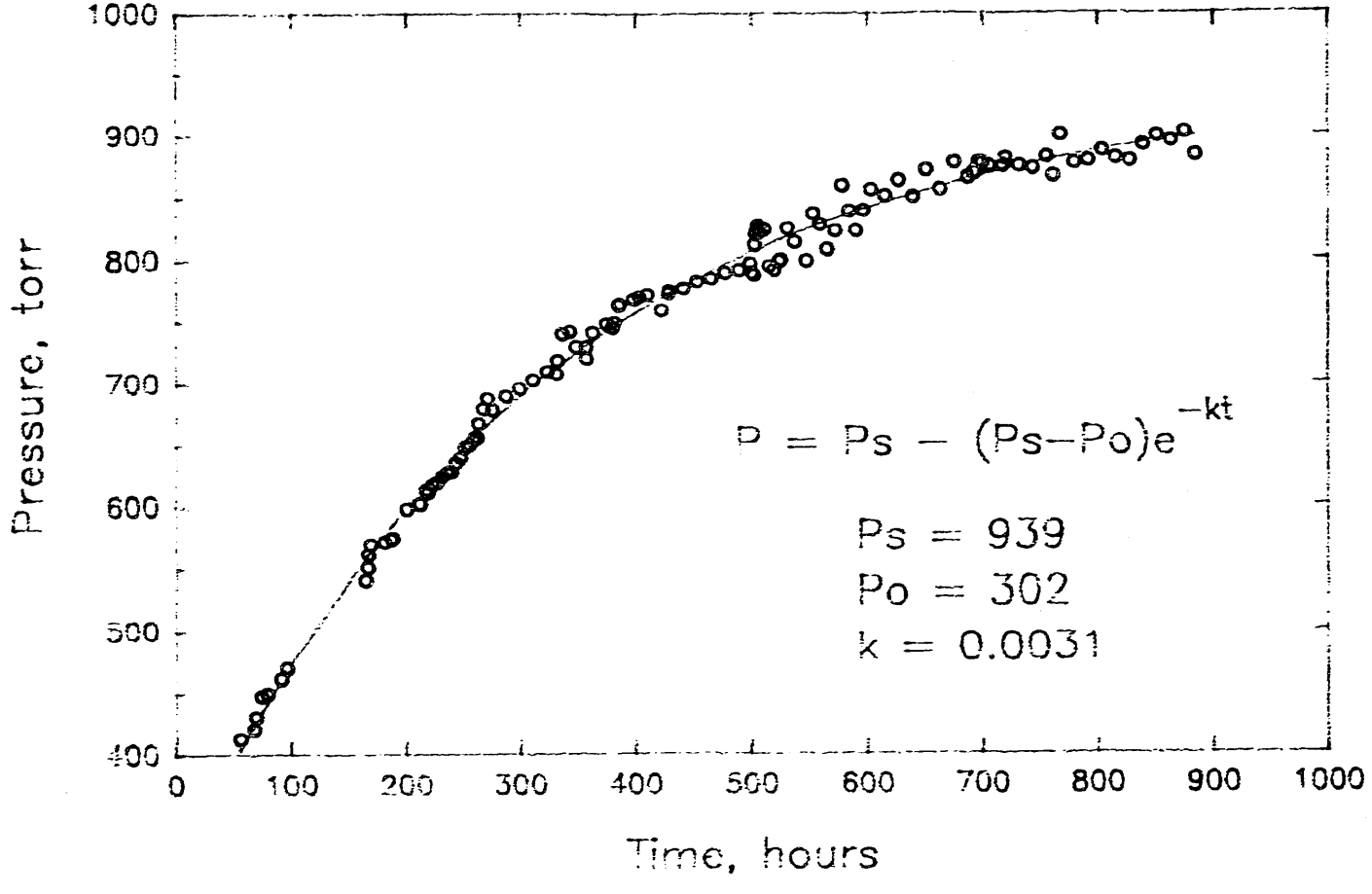
* All results based on weight of sample as received.



Test Apparatus

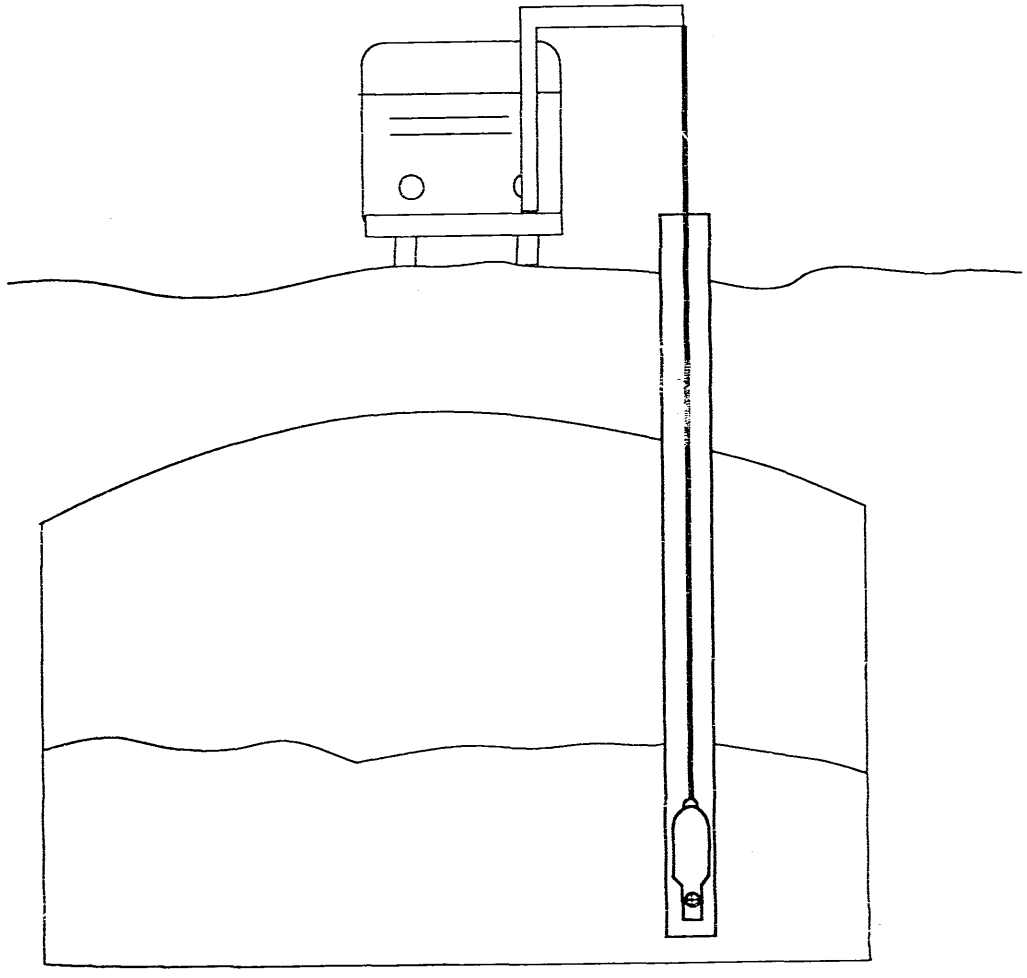
Figure 1

EDTA/HEDTA, ALL DATA



ATTACHMENT F

Liquid Observation Wells



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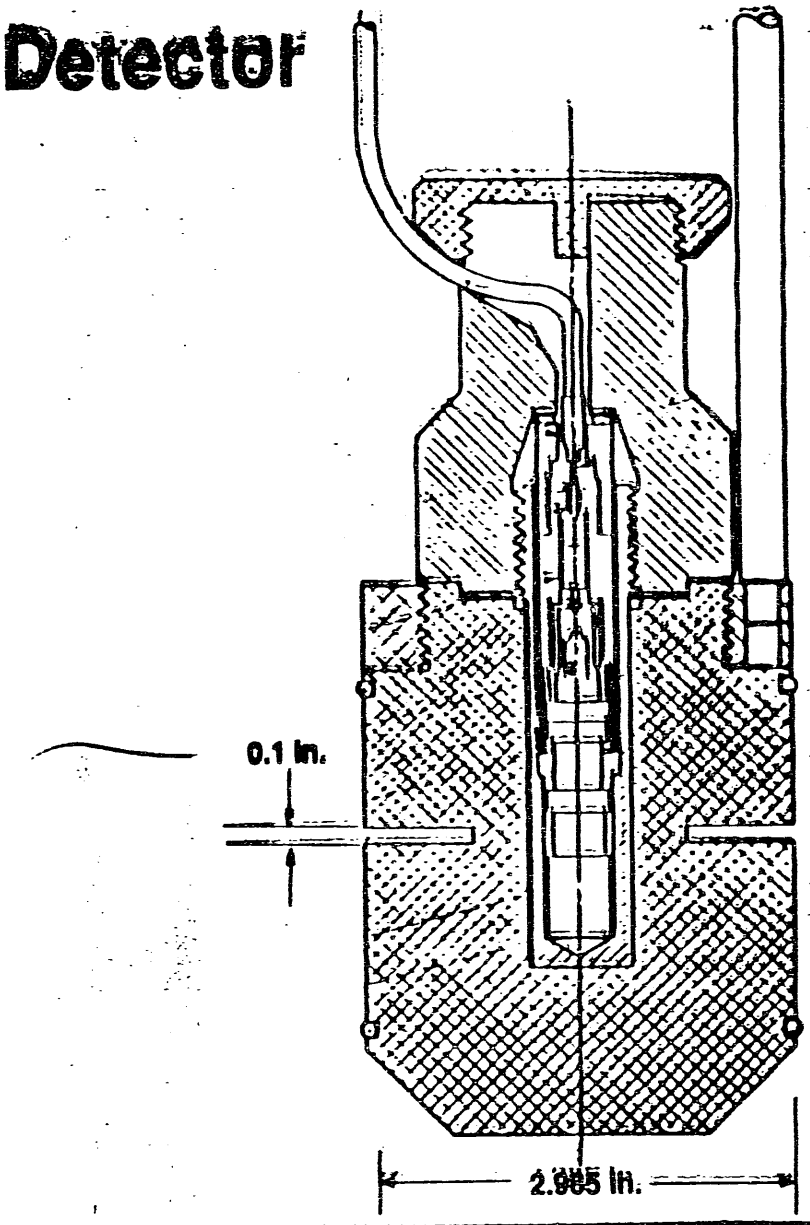
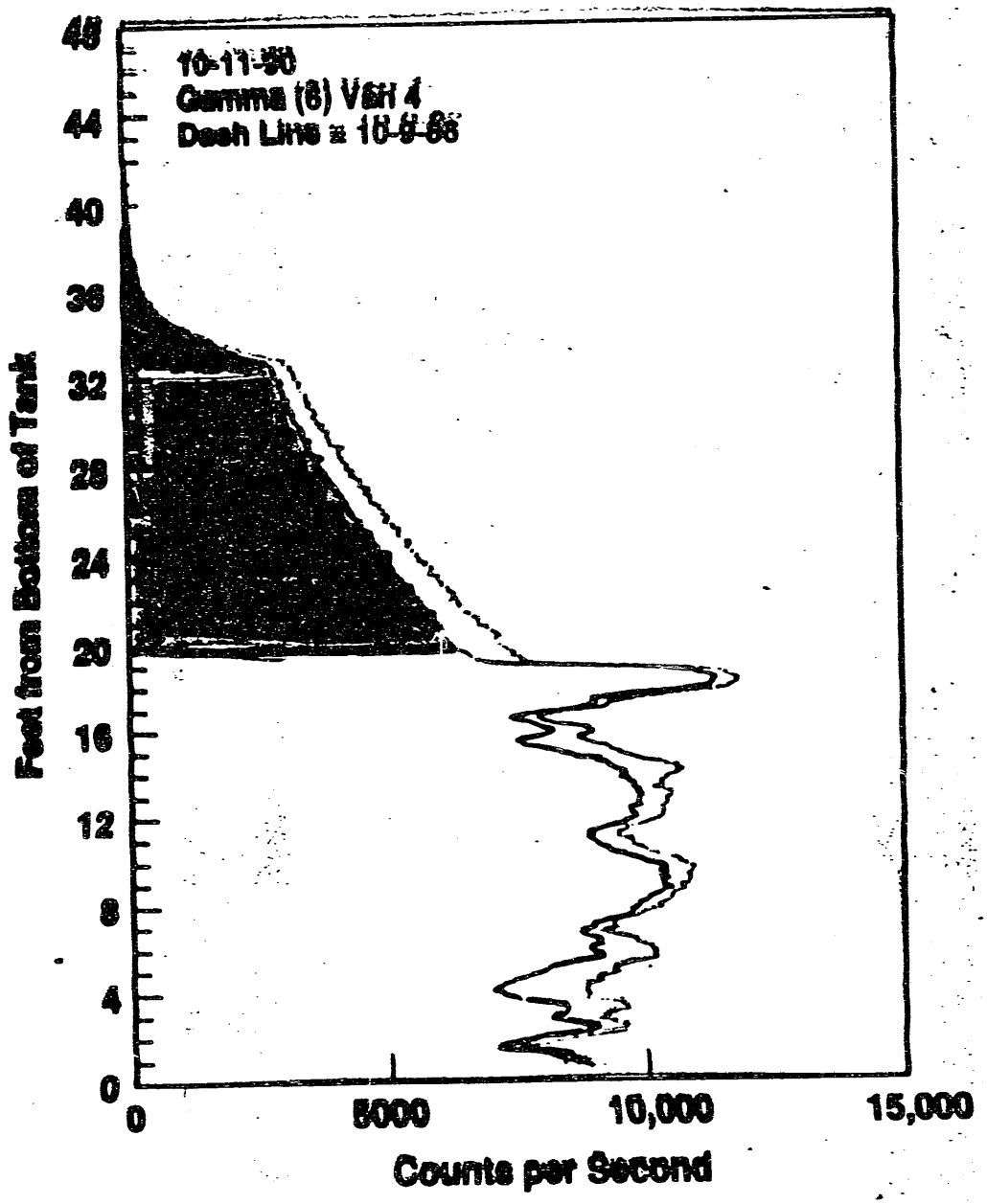
Gamma Detector

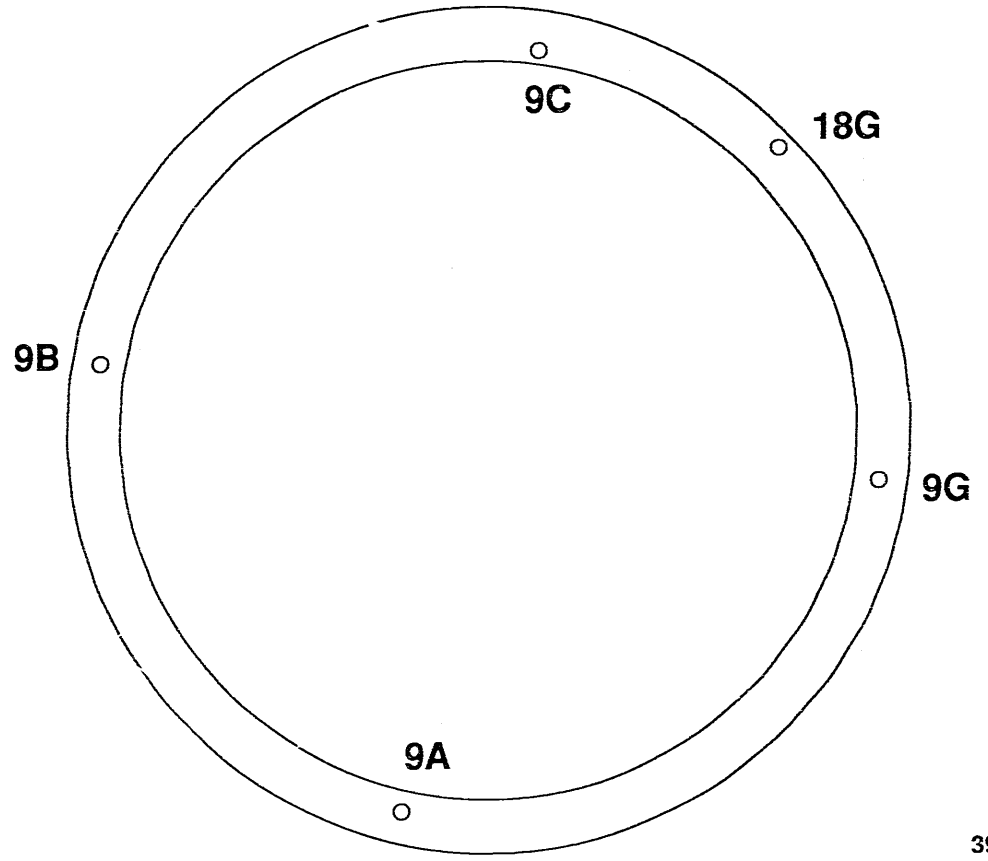


Tank 106-BY (66)



5/10/92 1.14

Tank 101-SY
Riser Location



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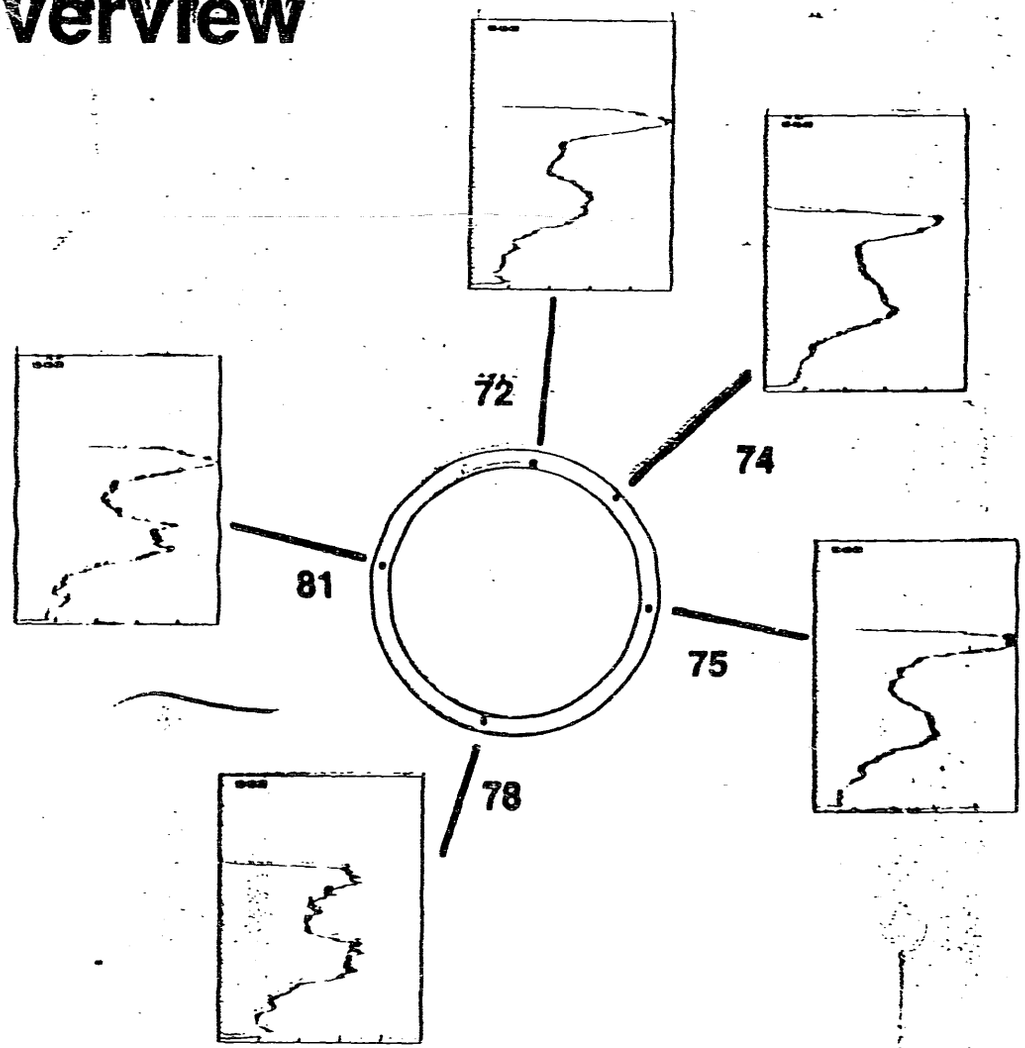
Data Overview



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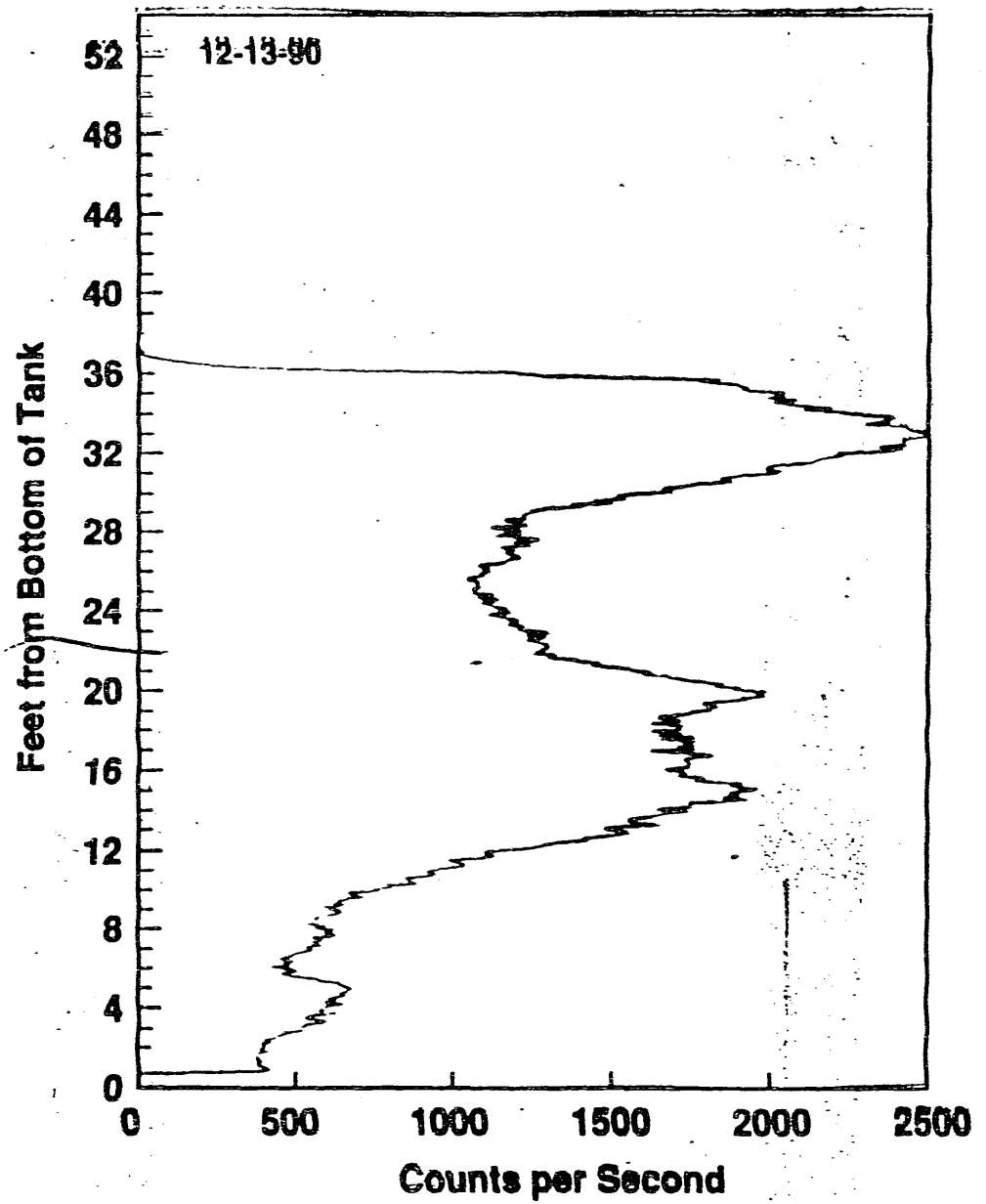

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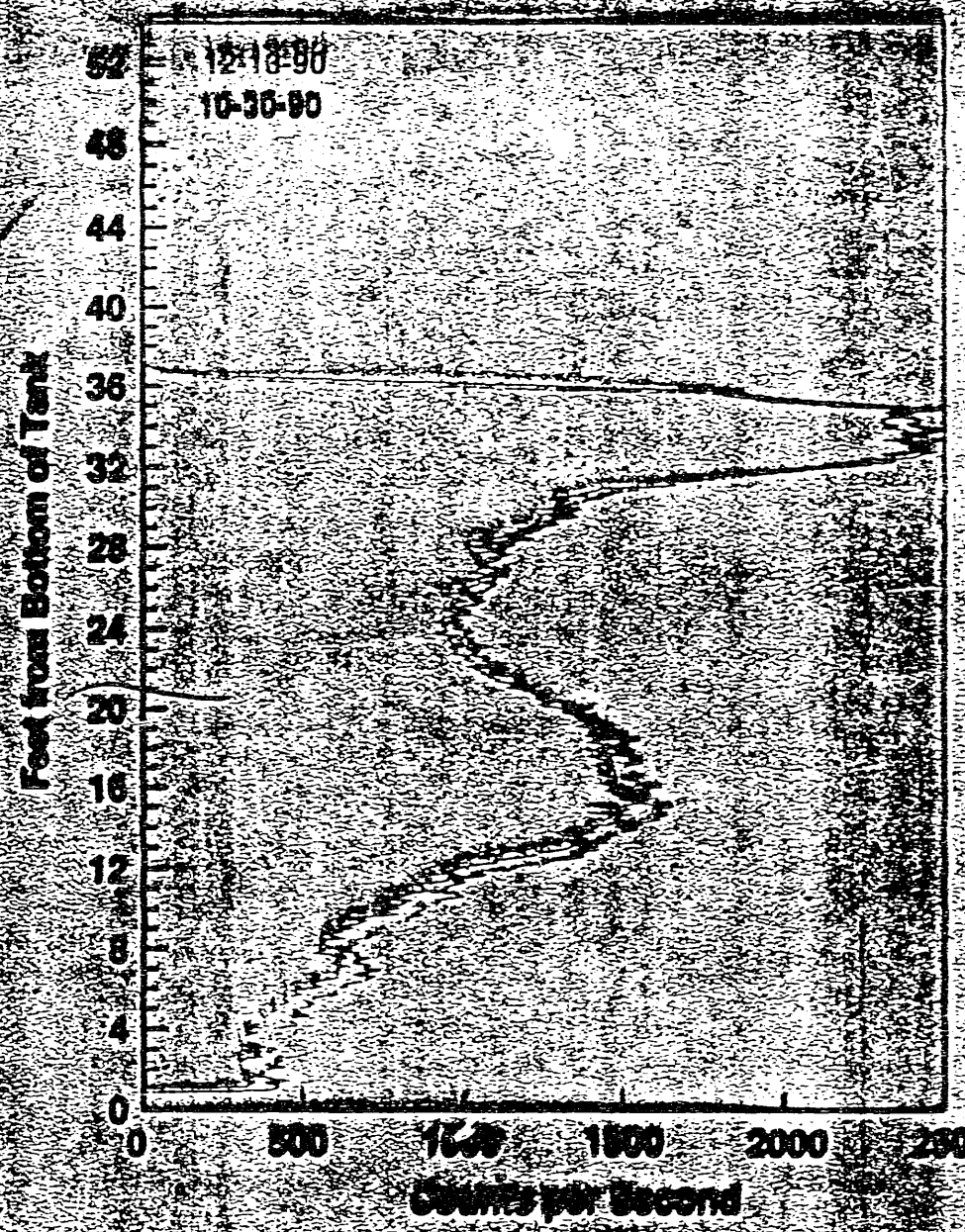
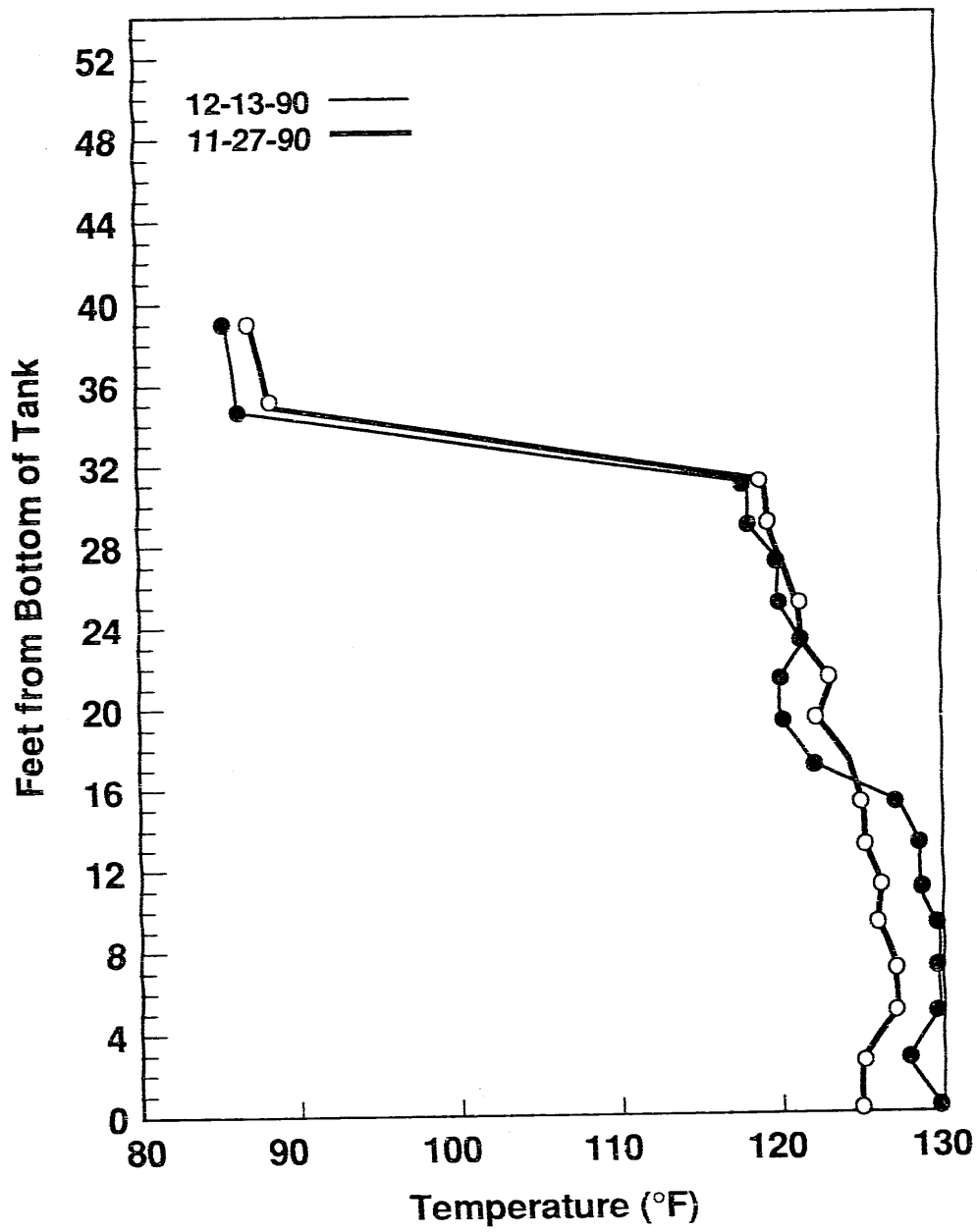
F.6

Tank 101-SY (75)



F.7

Tank 101-SY Temperature Profile



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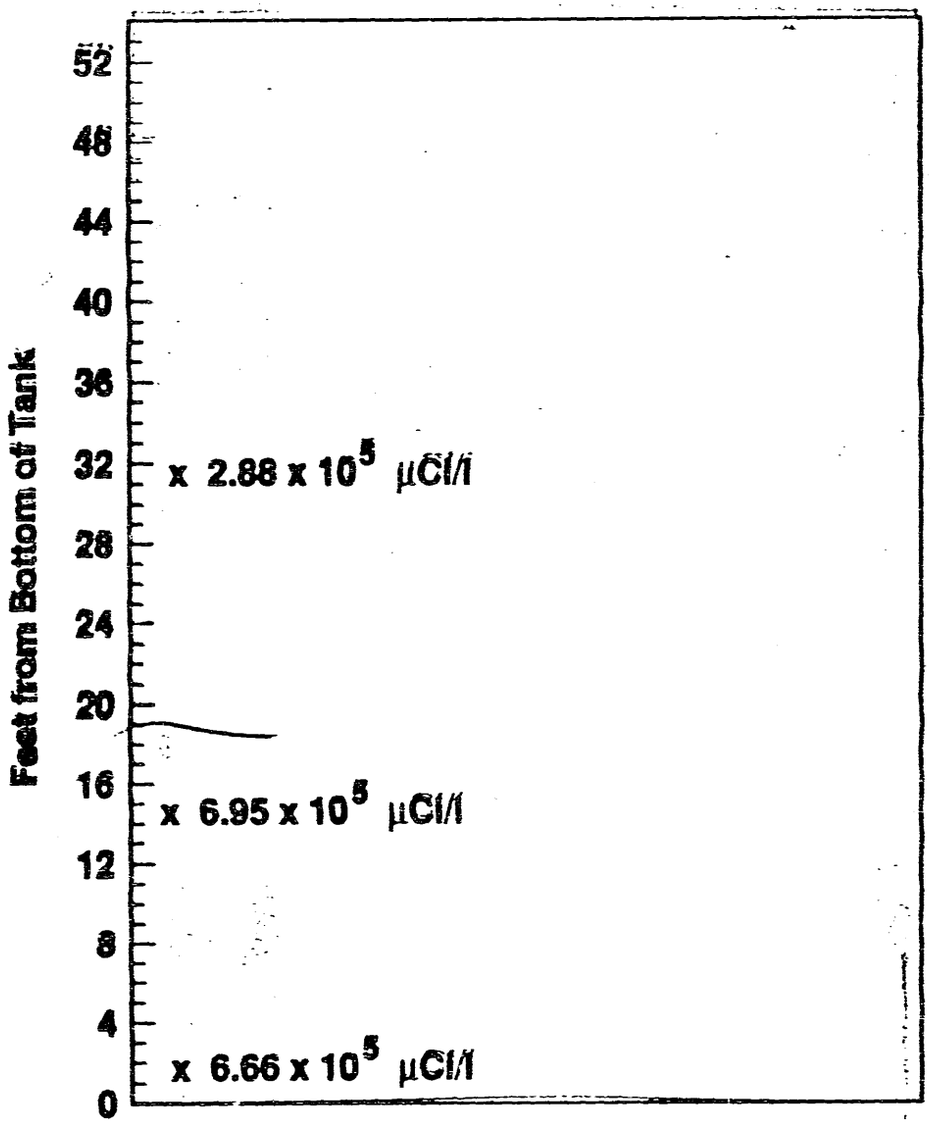
Tank 101-SY



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October 24, 1990 Event Summary

TIME: 0604 HRS (CASS Time)

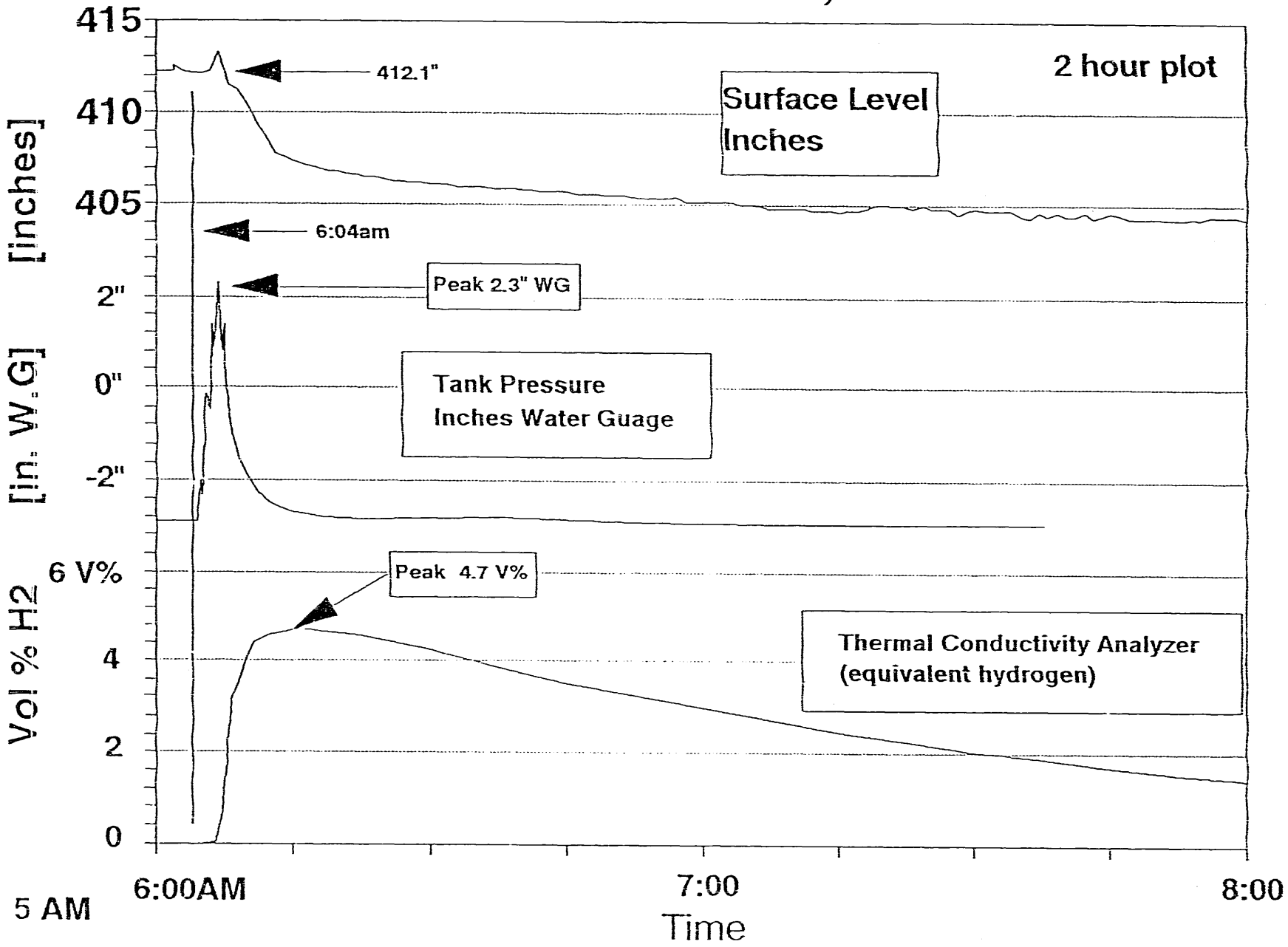
SURFACE LEVEL CHANGE: 412.1 inches to 402.9 inches
(Max. 413.2 inches at 0607 hrs)

PRESSURE: Normal -2.9 inches Max. +2.3 inches

TEMPERATURE: Upper increased 8° - 15°F
Middle increased 4°F
Bottom decreased 6° - 12°F

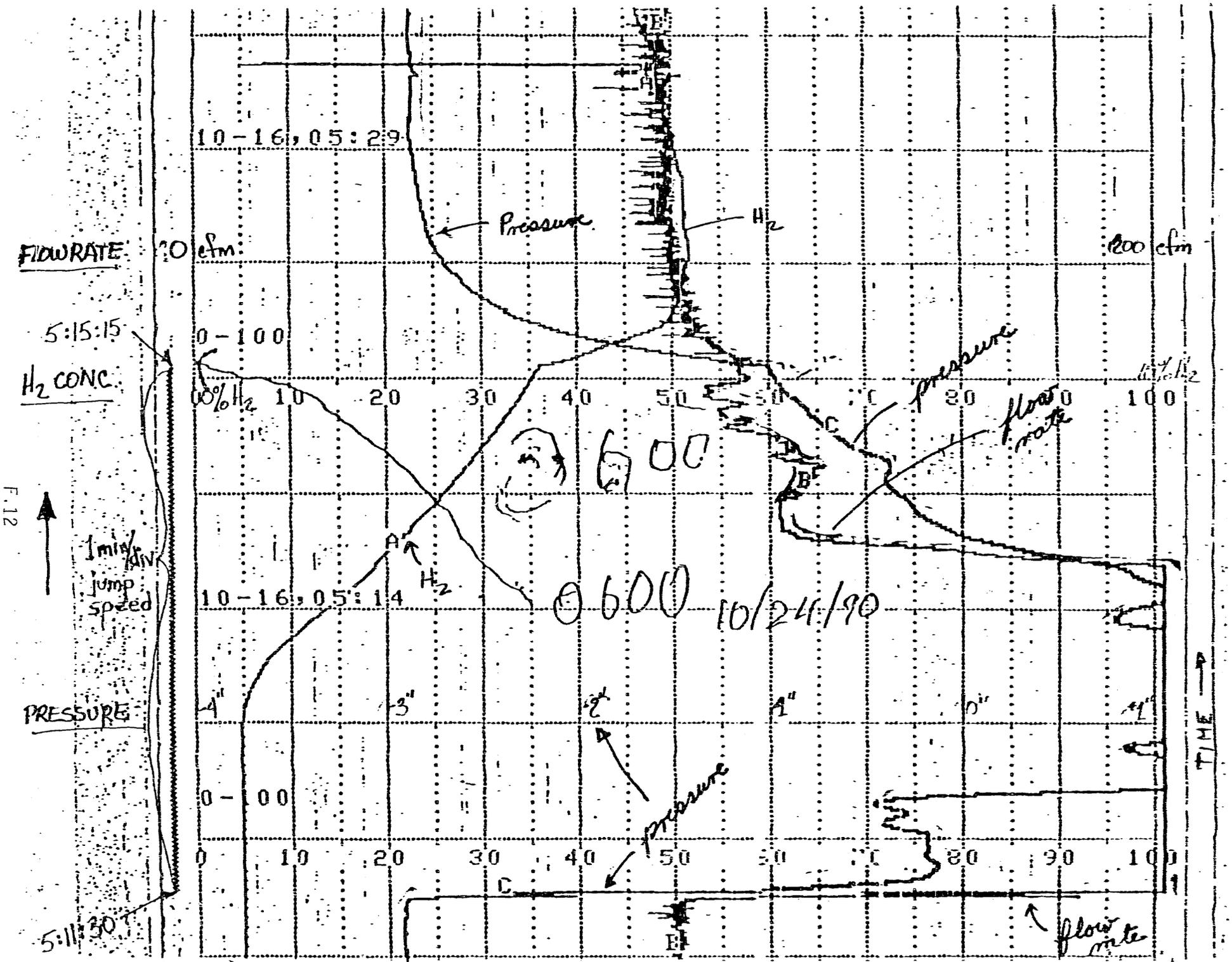
HYDROGEN: 4.7% Thermal Conductivity at 0615 hrs
4.6% Gas Chromatograph at 0616 hrs
4.5% Mass Spectrometer at 0625 hrs

241-SY-101 October 24, 1990 Event

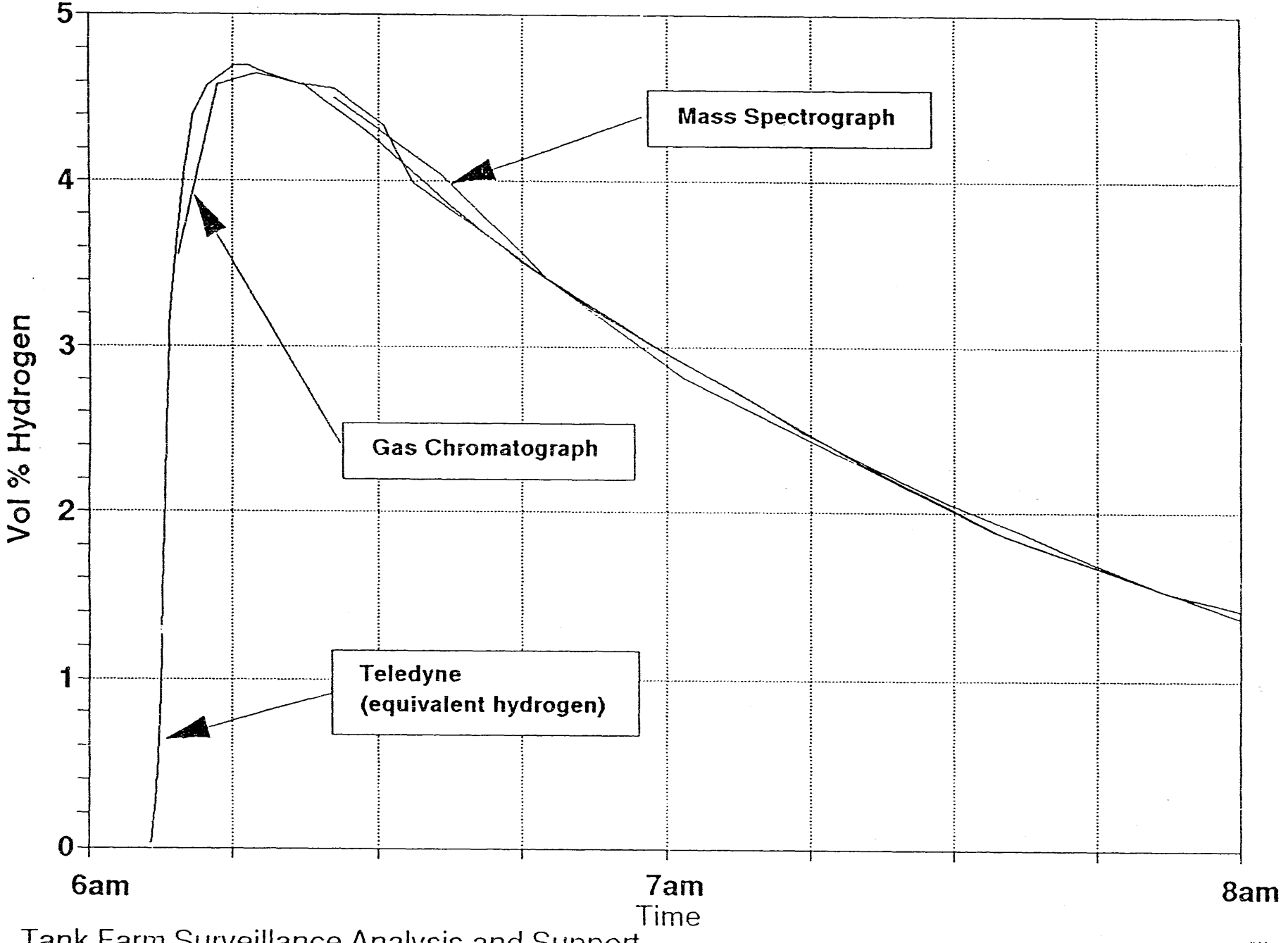


Tank Farm Surveillance Analysis and Support

sl/p/td-oct-12h


FLOWRATE
0 cfm
200 cfm
5:15:15
H2 CONC.
0-100
0% H2
100% H2
10-16, 05:29
10-16, 05:14
Pressure
H2
pressure
flow rate
1 min/div
jump speed
PRESSURE
-4"
-3"
-2"
-1"
0"
+1"
0-100
5:11:30
TIME
0600
0600 10/24/90

241-SY-101 Oct 24, 1990 Gas Venting- Hydrogen Measurements



Tank Farm Surveillance Analysis and Support

all H oct 21

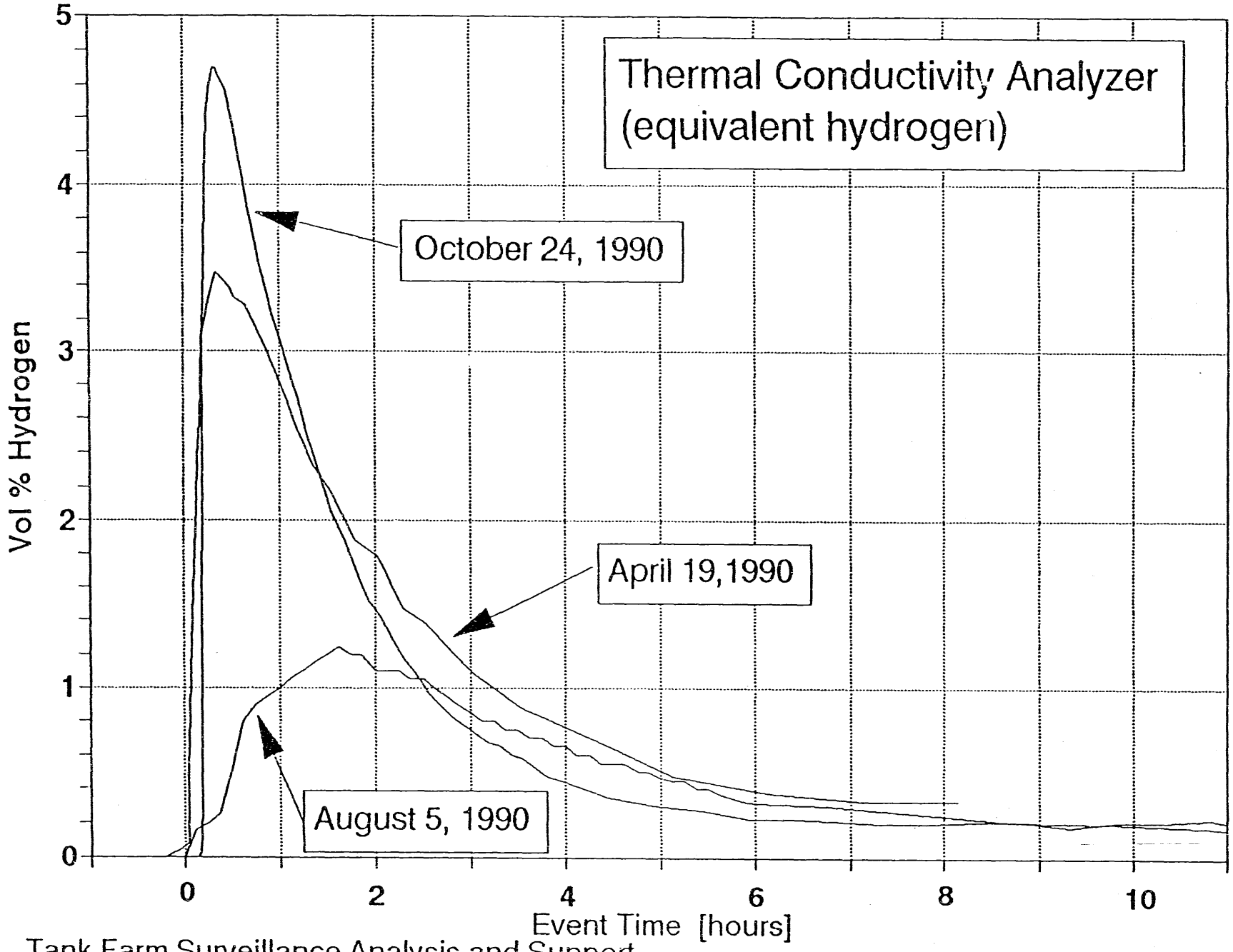
Comparison of Last Three Events by Predictive Computer Model

	Duration	Calculated Hydrogen Conc.(Measured)	Gas Volume*	
April 19, 1990	20 min.	** (3.5%)	7300 ft^3	11000
August 5, 1990	3 hrs.	0.8% (1.25%)	3400 ft^3	7000
October 24, 1990 (preliminary results)	5 minutes	4.9% (4.8%)	7000 ft^3	10000

* Volume during increased pressure period. Total gas volume for events are greater.

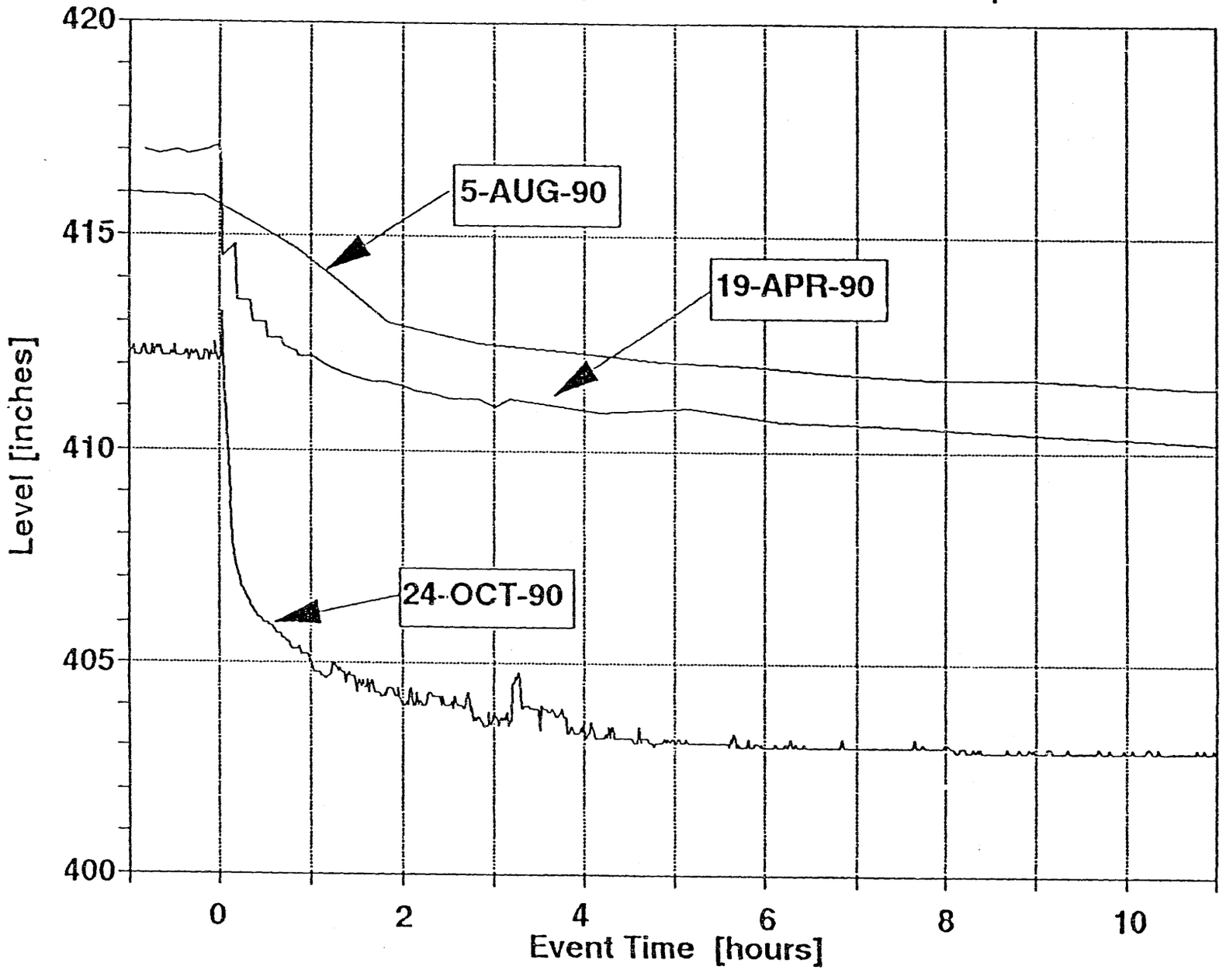
** Calculated concentration ranges between 3.9% and 4.9 % depending on assumptions for gas injection rate.

241-SY-101 Gas Venting- Hydrogen Concentration Comparisons

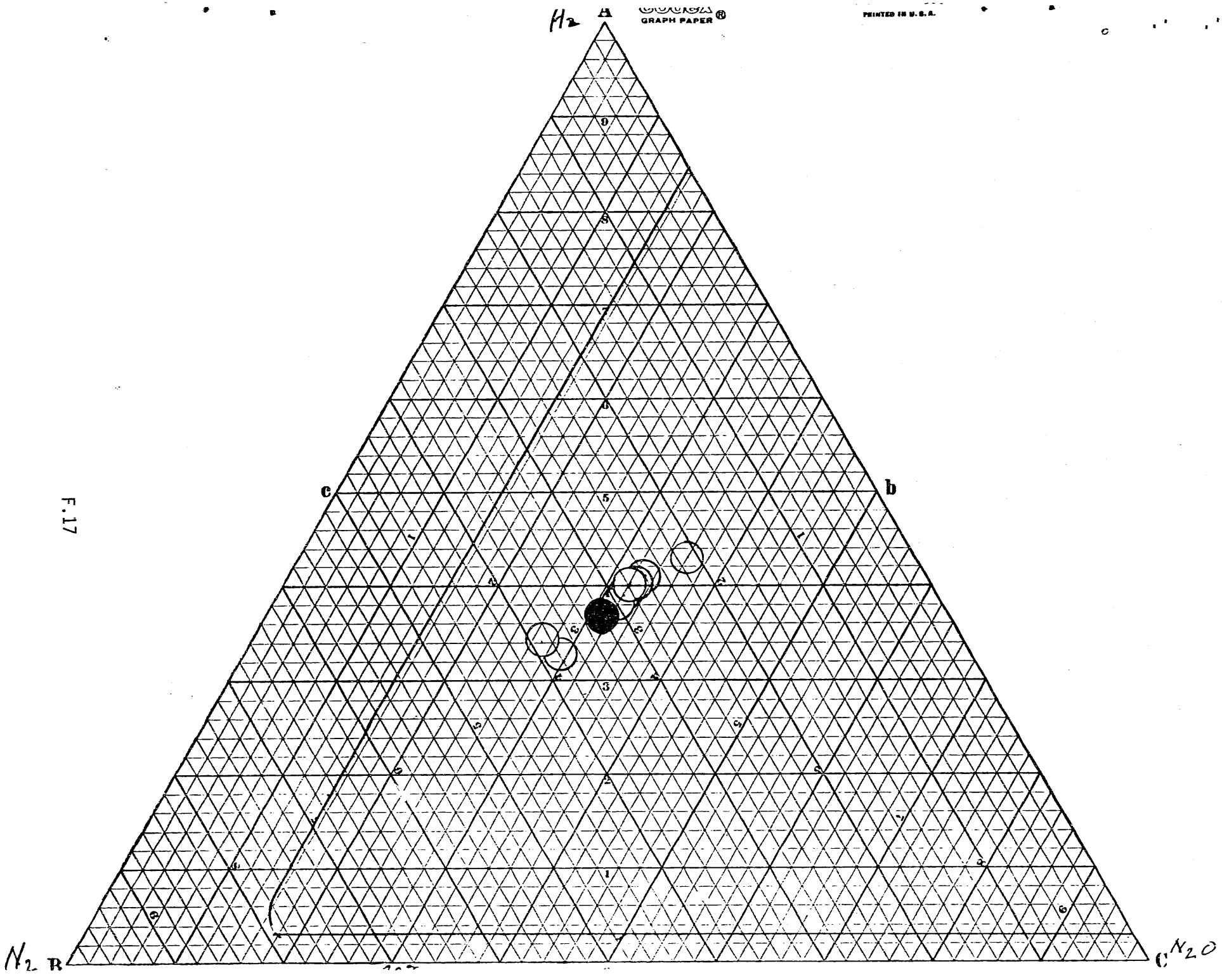


Tank Farm Surveillance Analysis and Support

241-SY-101 Gas Venting- Surface Level Comparisons



Tank Farm Surveillance Analysis and Support



F.17

ATTACHMENT G

SY-101 CHEMISTRY MODELING EXPERIMENTS

D. D. Siemer, WINCO

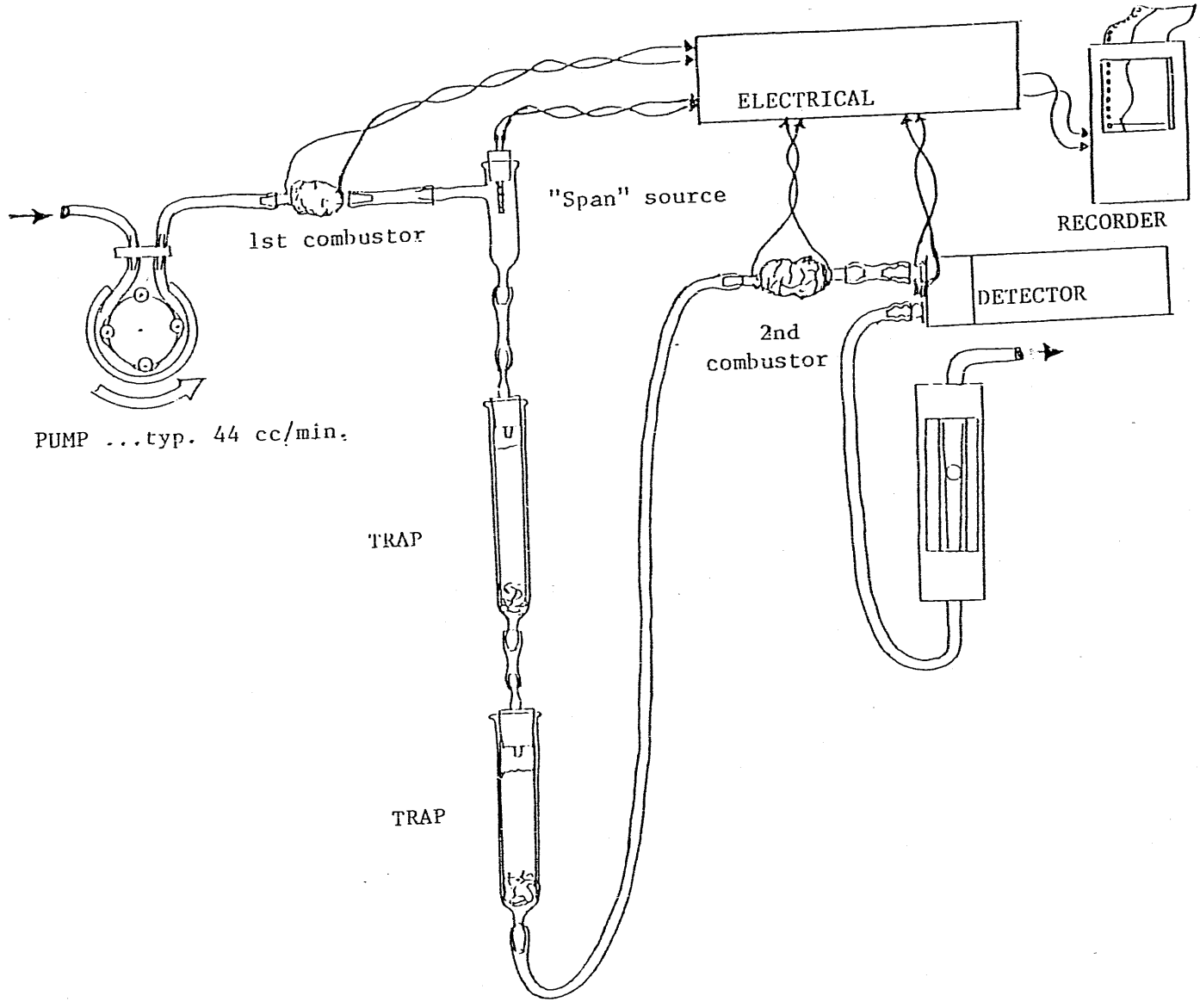
G.1

H_2 GENERATION RATE WAS SOLE MEASURE OF REACTION RATE

SMALL-SCALE EXPERIMENTS RUN UNDER MODERATE CONDITIONS

IMINODIACETIC ACID (IDA) USED AS MODEL "ORGANIC"

BASIC OUTLINE OF HYDROGEN MONITOR



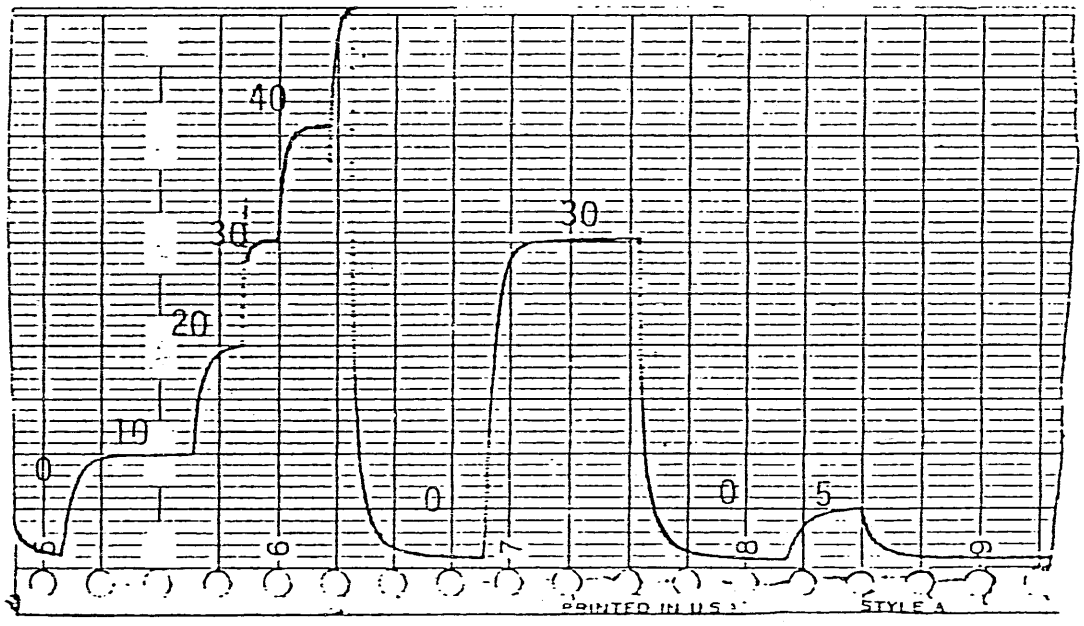


Figure 5: Chart recording showing the response of a 0 to 50 ppm-scaled monitor to various hydrogen concentrations. The detection cell's working electrolyte was generated by electrolyzing 2.5 uL of phosphoric acid. Time divisions are 15 minutes.

HYDROGEN MONITOR'S SPECIFICITY

1. Trap efficiency - combination of ambient-temperature molecular sieve & activated carbon traps will stop virtually anything capable of being oxidized to water vapor.

2. Selective combustion catalysts

   Ag_2O on Chromosorb A ... selective for H_2 vs propane

   CuO on Chromosorb A ... non-selective but requires no O_2 in carrier

   Pd/Ru/Pt ... non-selective & easily "poisoned"

3. Chromatographic effects - with any reasonable choice of trapping agents, hydrogen will get to the combustion catalyst/detector cell long before any conceivable interferent could: in "batch analysis" mode, hydrogen gives a sharp peak response ... nothing else can do that.

SENSITIVITY

1 UA = 5.18 E-12 moles/sec of H2

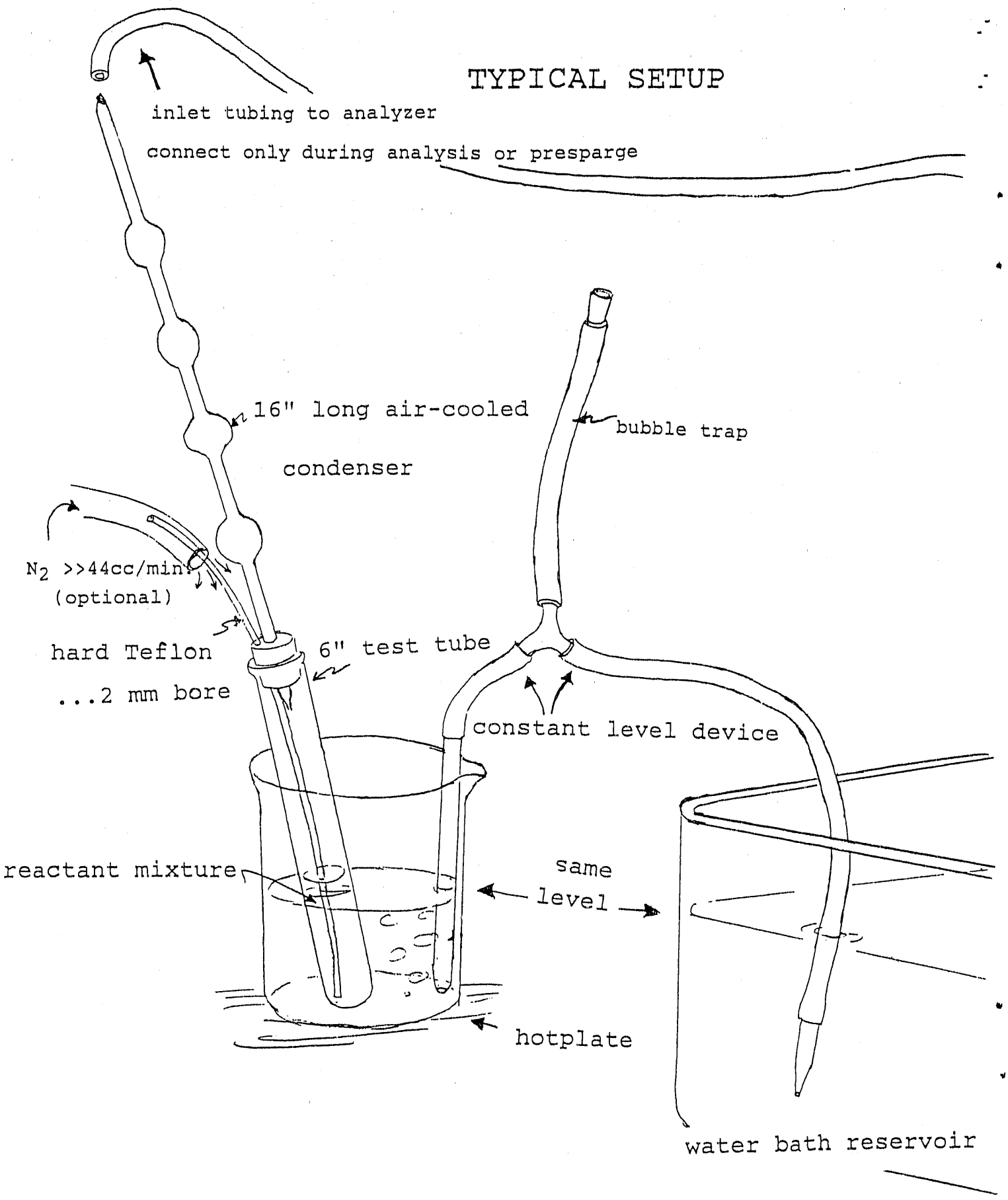
= 0.42 uL per hour H2

"Noise " - short-term (approx. minute to minute)

noise is 1 ua maximum

(approx. 0.16 ppm H2 at 44 cc/min)

SY-101 generates about 0.053 ua's worth of H2 per cc of waste


TYPICAL SETUP
inlet tubing to analyzer
connect only during analysis or presparge
16" long air-cooled
condenser
bubble trap
N_2 >>44cc/min
(optional)
hard Teflon
...2 mm bore
6" test tube
constant level device
reactant mixture
same
level
hotplate
water bath reservoir

TWO WAYS OF DOING EXPERIMENTS

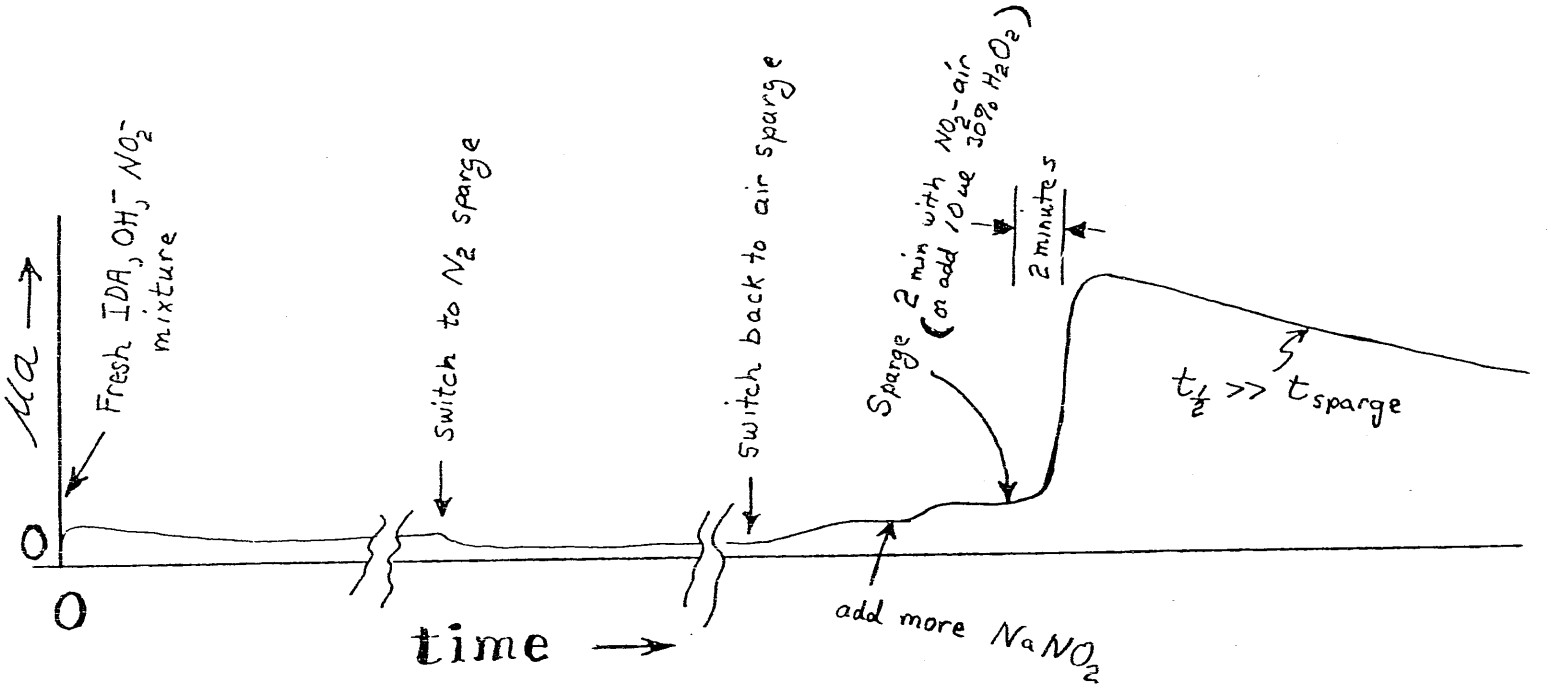
CONTINUOUS: monitor H_2 in sparge gas continuously passed through a single batch of reactant solution - vary reaction conditions & note any change in current response...used in initial "scoping" work but is slow & subject to baseline "drift" errors.

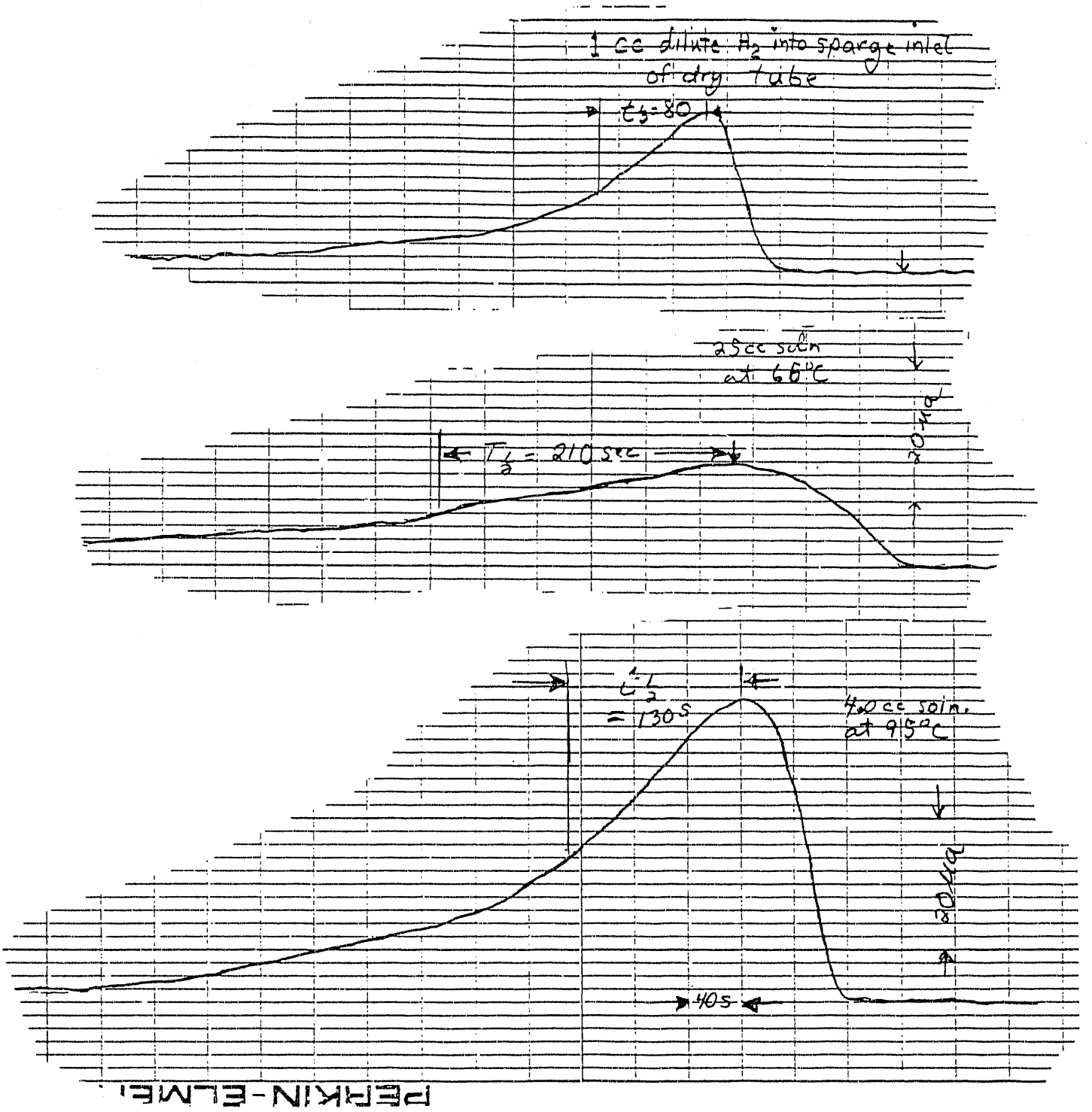
BATCH: prepare parallel batches of reactants varying one parameter & keeping all others constant. Run reactions simultaneously and periodically determine accumulated hydrogen in each vessel by sparging them and integrating the coulometric response...much more efficient way to do experiments.

TYPICAL "CONTINUOUS" EXPERIMENT

NO_2/H_2O_2 ADDITIONS (added through "belled" purge tube)

Conclusions: NO_2 & peroxide are especially efficient oxidants





HYDROGEN IS QUITE SOLUBLE IN REACTION MIXTURES

CONCLUSIONS DRAWN FROM "SCOPING" STUDIES

1. OXIDANT NEEDED TO PRODUCE H_2 FROM MOST "ORGANICS" (NO_2 is especially potent)

2. ADDING MORE BASE <u>ALWAYS</u> INCREASES H_2 PRODUCTION

3. ESPECIALLY REACTIVE "ORGANICS" INCLUDE GLYCOLIC ACID TWO DIFFERENT ~~GEM~~ 1-3-DIOLS, DEXTROSE, AND GLUTARALDEHYDE... ACETIC ACID, BENZOIC ACID, FORMIC ACID, PRIMARY ALCOHOLS, & BENZALDEHYDE GAVE NO H_2...IDA AND EDTA GAVE SMALL BUT NON-ZERO RESPONSES...HEDTA CONSIDERABLY MORE ACTIVE

4. FORMALDEHYDE IS "SPECIAL" IN THAT IT PRODUCES H_2 RAPIDLY WITH SIGNIFICANT CHEMICAL YIELD IN THE ABSENCE OF AN OXIDANT.

5. ALUMINUM SEEMS TO BE UNIMPORTANT

WHY IDA?

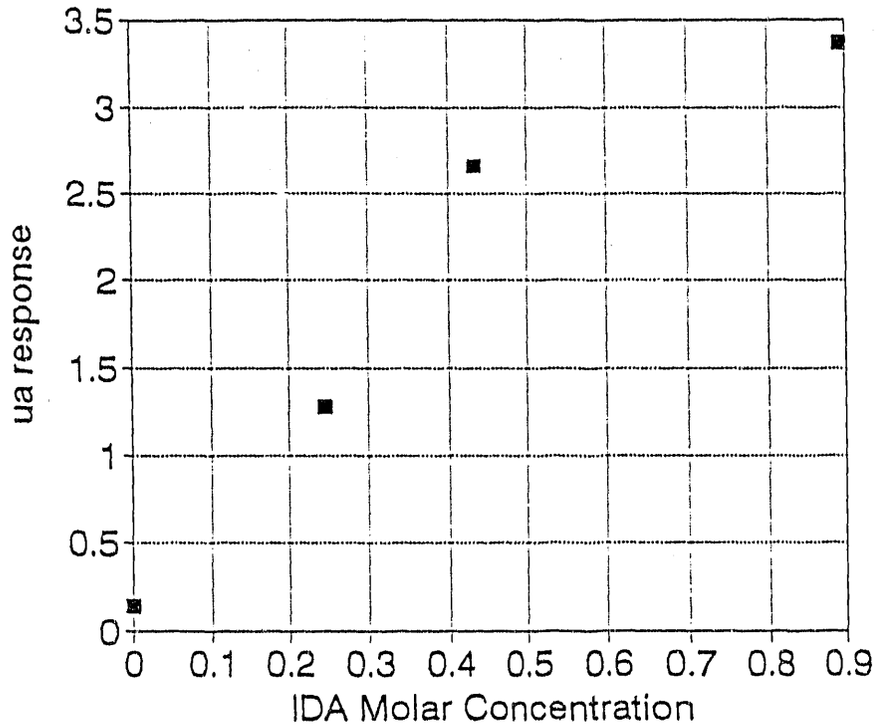
IT's "CONSERVATIVE"

IT'S A MAJOR DECOMPOSITION PRODUCT OF ORIGINAL CHELANTS

MORE REACTIVE ORGANICS ARE PROBABLY GONE BY NOW
(Strachan et al. 1986)

IDA Concentration vs Response

Nitrite 3.07 M, free OH 3.0 M

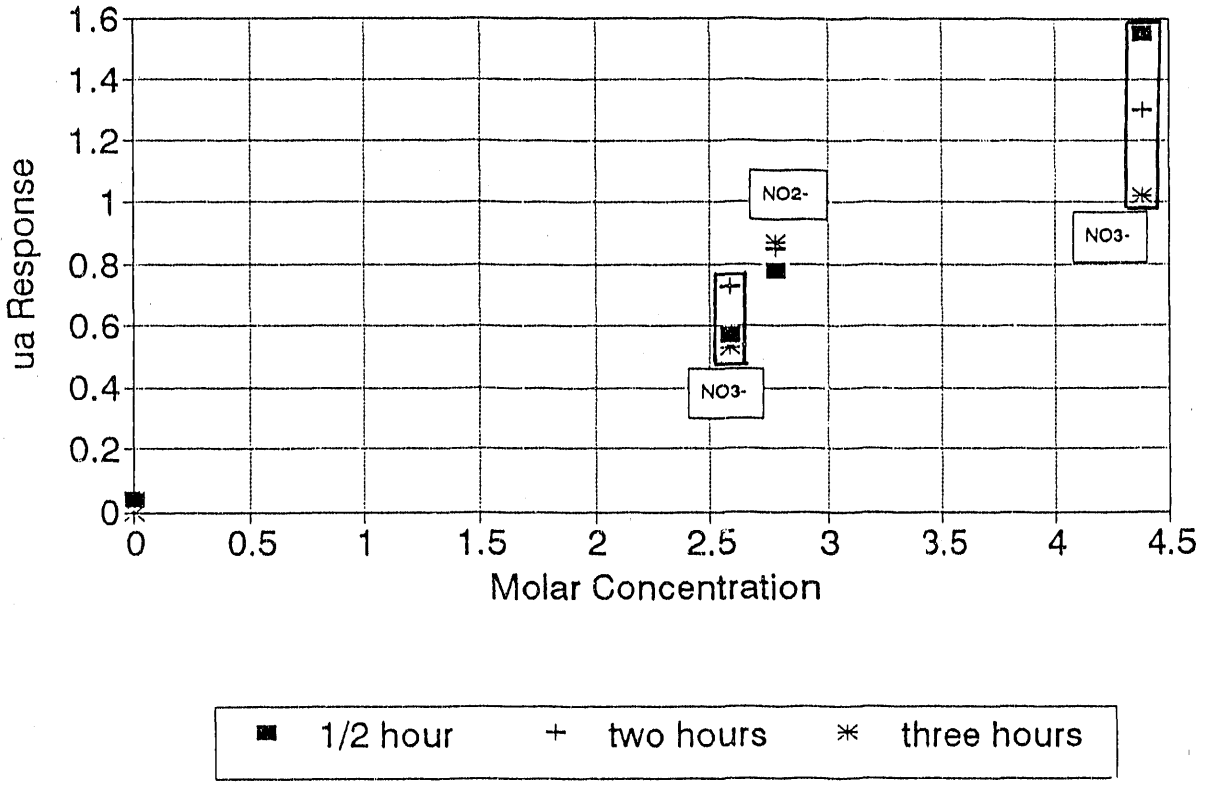


THE EXPERIMENT: A "mother solution" of NaOH and $NaNO_2$ in water was prepared. Another solution of IDA and an equivalent amount of NaOH was also prepared. Various volumes of the second solution were added to fixed volumes of the first in four tubes and then the liquid volumes were made up to a constant 4 cc. The tubes were thermostatted at 95 C, sparged with air, and the hydrogen so-generated "batch analyzed".

CONCLUSION: Reaction is first order in [IDA]

Nitrate/Nitrite Conc. (M)

OH = 3 M, IDA=0.45 M (4 cc)

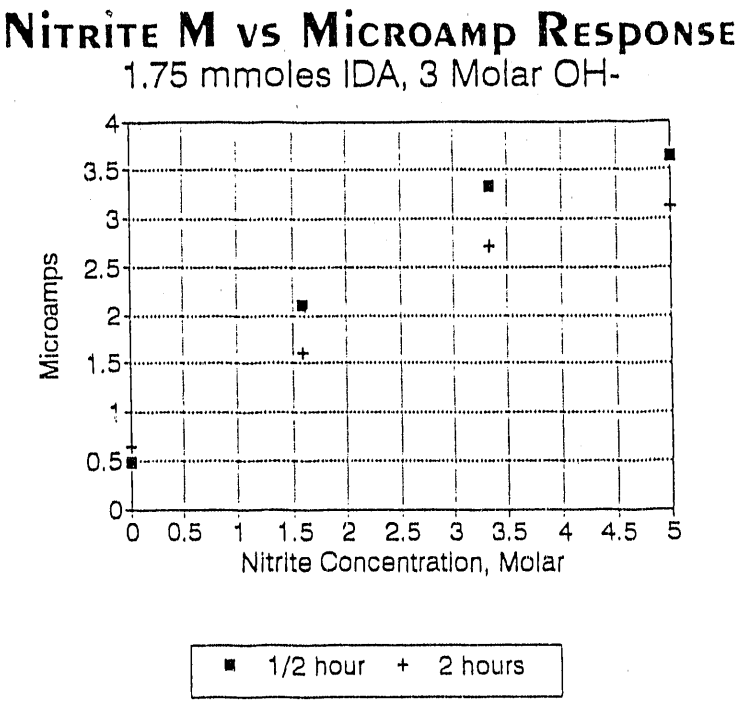


THE EXPERIMENT: A "mother solution" containing IDA dissolved in excess NaOH was divided among four test tubes. Two different amounts of $NaNO_3$ were added to two of the tubes and $NaNO_2$ was added to another. Volumes were adjusted to a common value with water. The tubes were thermostatted at 95 C and the hydrogen generation rate determined.

CONCLUSION:

1. Rate is proportional to nitrate conc.

2. nitrite is somewhat "stronger" than nitrate.



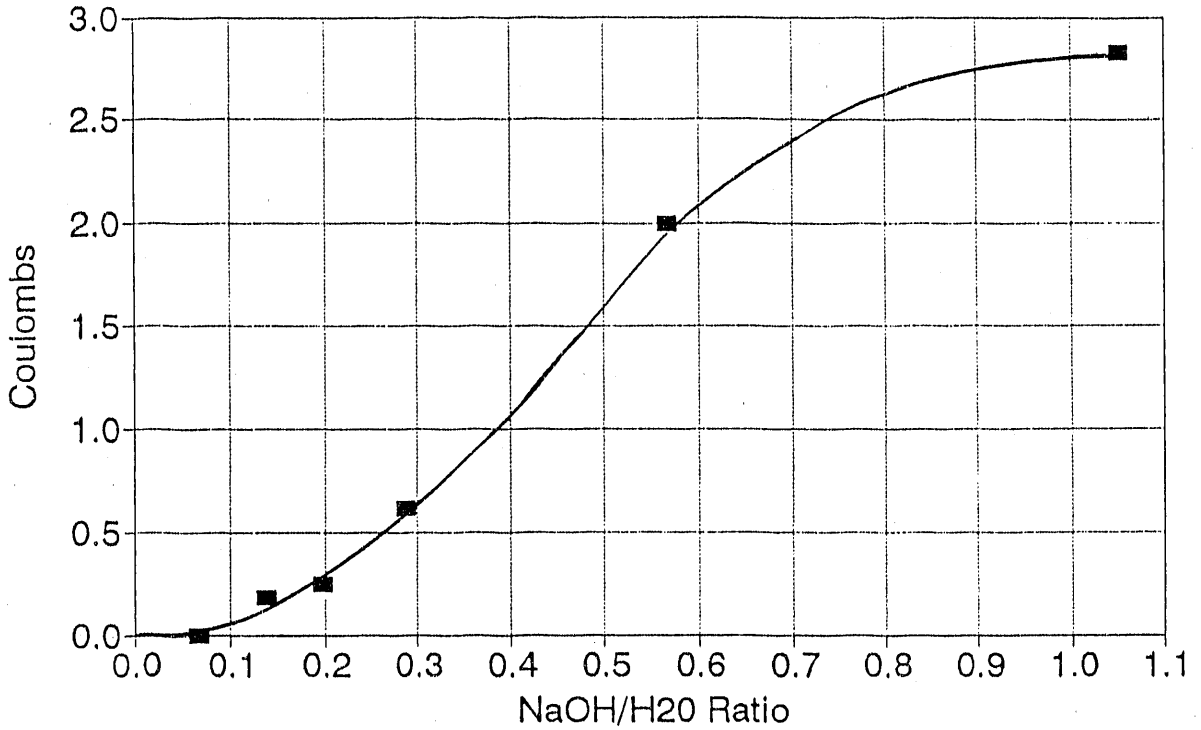
THE EXPERIMENT...A "mother solution" containing IDA dissolved in excess NaOH was divided among four test tubes. Various amounts of $NaNO_2$ were added to the tubes and volumes were adjusted to a common value with water. The tubes were thermostatted at 95 C and the hydrogen generation rate in each determined.

CONCLUSION:

H_2 generation is 1st order in NO_2^-.

Effect of OH on Hydrogen Response

5 uL Formalin-continous sparge



THE EXPERIMENT: 5 uL aliquots of 37% HCOH were added to thermostated test tubes containing various concentrations of NaOH. The solutions were continuously sparged (44 cc/min) with air and the H_2 in that air monitored. The coulombic response at each [OH] conc. is shown in the plot. Maximum chemical yield noted was 26%. A subsequent repeat of the experiment at one [OH^-] level using nitrogen instead of air gave similar results.

observation: the H_2 peaks seen for low [OH^-] concs. were very low and broad...at high [OH^-], the peaks were not only much larger but also much narrower.

CONCLUSIONS:

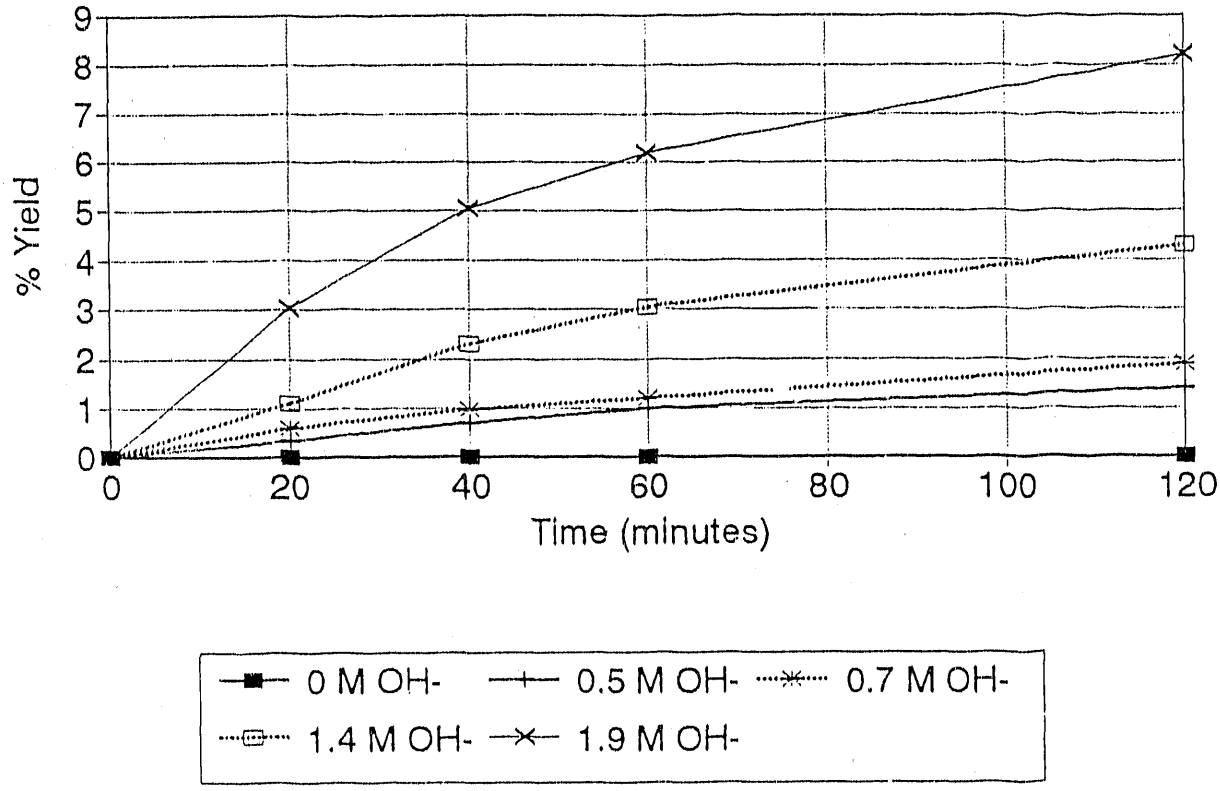
1. Formaldehyde produces hydrogen fairly efficiently at high OH^- concentrations

2. Both the chemical yield and rate are sensitive to [OH^-]

3. No oxidant is required to produce H_2 from HCOH.

% Hydrogen Yield vs Time

5 umoles HCOH, 3.85 M NO3-



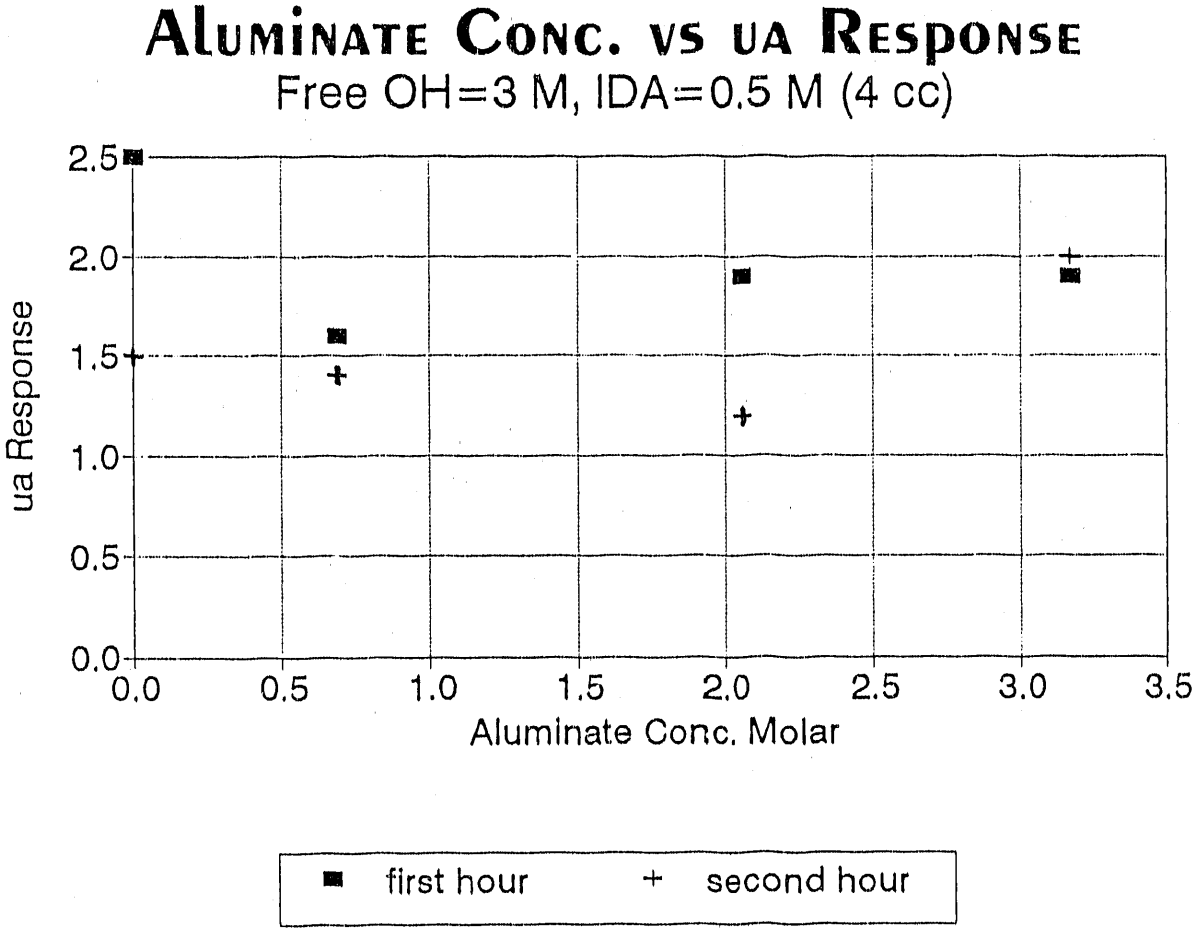
THE EXPERIMENT: formaldehyde was added to test tubes containing various amounts of NaOH and a constant 3.85 M nitrate. The tubes were thermostatted and any accumulated H_2 "batch determined" at various times. The plot shows total H_2 generated as a function of time. After two hours, enough NaOH pellets were added to tube #1 to raise free [OH] from 0 to >10 M...a huge peak immediately appeared which integrated out to a coulombic response corresponding to an 85% yield.

CONCLUSIONS:

1. Chemical yield is strongly dependent on $[OH^-]$

2. Rate of hydrogen generation is also strongly dependent on $[OH^-]$

2. Formaldehyde (or the "real" H_2 precursor derived from it) is not very volatile and is stable in absence of free hydroxide.



THE EXPERIMENT: A "mother solution" of $Al(OH)_3$ and excess NaOH was first prepared. Various amounts of that solution were dispensed into four tubes. 0.26 g. of IDA was added to each tube and enough NaOH was added to bring free $[OH^-]$ to a common value. Then 0.82 g. of $NaNO_3$ was added to each tube and the volumes adjusted to 4 cc. The tubes were then thermostated at 95 C and the hydrogen generation rates measured after one and two hours.
(Free OH = [total OH] - 2 [IDA] - $[Al(OH)_3]$)

CONCLUSION

Aluminum plays no part in H_2 generation from IDA

TEMPERATURE EFFECT EXPERIMENT

prepare large volume of 4.08 M $NaNO_2$, 4.86 M OH^-, 0.65 M IDA^{-2}

place 4.72 g. into small tube

put 34.6 g. into a large tube

insert condenser/stopper &

thermostat at 95°C

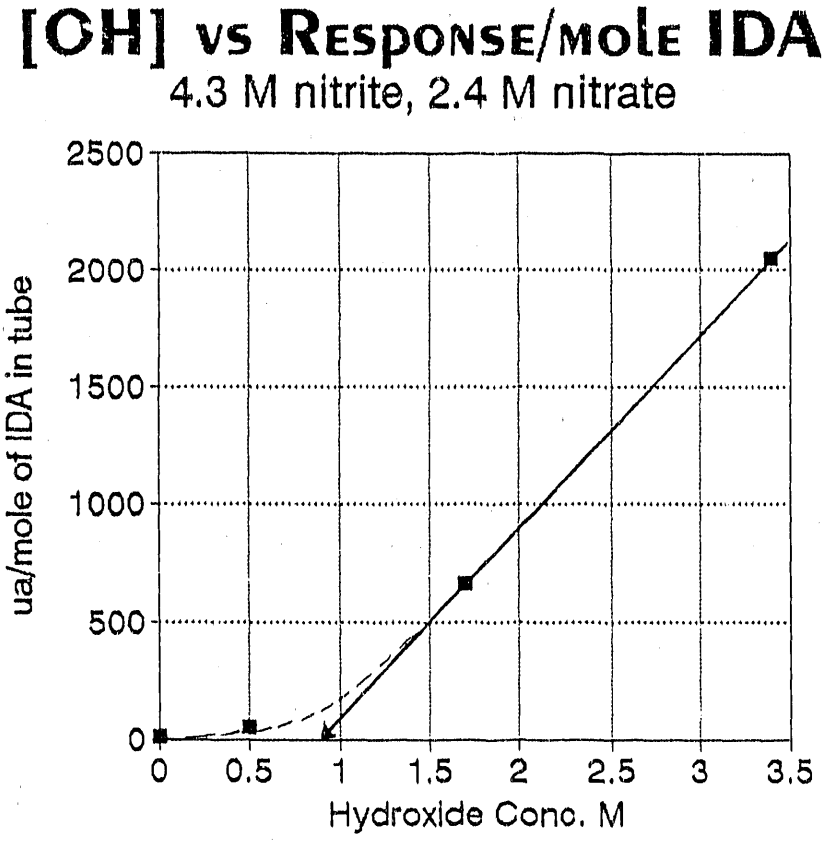
thermostat at 66°C

periodically determine accumulated H_2 & calculate response current

TIME(hrs)	ua (95°C)	ua (66°C)	E_a(Kcal/mole)
0.5	4.24	1.86	24.1
	(air sparged)		
1.5	4.38	2.16	23.1
3	1.83	1.10	21.4
	(N_2 sparged)		
6	1.49	0.87	21.7
23	4.48	1.92	24.3
	(air sparged)		
24	4.84	2.25	23.6

$\Sigma x/6 = 23.0$ Kcal/mole

rate 95°C/rate 56°C(SY 101's temp.) = 41:1



THE EXPERIMENT: A "mother" solution containing IDA, excess NaOH, and $NaNO_2$ was "cooked" to > 240 C to simulate long-term reaction at 50-60 C. Then water was added along with enough HNO_3 to neutralize the "free OH". The solution was split among four tubes and various amounts of NaOH added. The tubes were sparged with N_2 & thermostatted at 95 C. The plot depicts hydrogen response vs $[OH^-]$ at 24 hours .

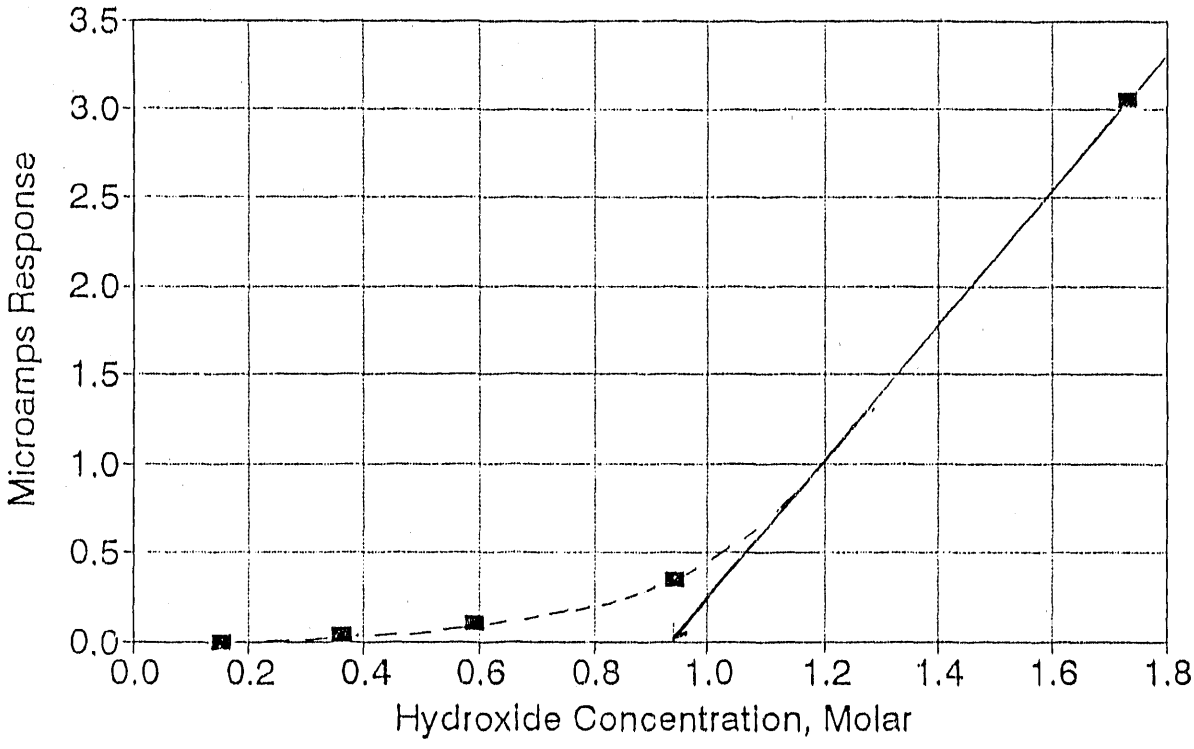
CONCLUSIONS:

1. Rate is very low below 1 M free OH^-

2. Rate prop. to [OH - "threshold level"]

Low Level Hydroxide Experiment

IDA=0.59 M, NO2-=4.3 M (after 24 hours)



THE EXPERIMENT: A "mother" solution containing IDA, sufficient NaOH to neutralize it, and $NaNO_2$ was prepared. The solution was divided into five tubes and various amounts of NaOH added. After diluting to a common volume (4 cc) the tubes were sparged with N_2 & thermostatted at 95 C. The plot depicts hydrogen response vs [OH] at 24 hours .

CONCLUSIONS:

1. rate is very low below 1 M free OH

2. OH^- "threshold level" is about 0.9 M

DILUTION EXPERIMENT

PREPARE A "MOTHER SOLUTION" WITH
0.43 M IDA^{-2}, 4.29 M OH^-, & 5.69 M nitrite

PLACE EQUAL VOLUMES (2.1 cc) INTO
EACH OF TWO TUBES

INCUBATE at 95°C, MEASURE ACCUMULATED H_2
& CALCULATE AVERAGE i

3.1 ua

3.0 ua
add 1.3 cc H_2O (TV=3.4 cc)

INCUBATE BOTH AT 95°C
MEASURE H_2, & CALC. i

1.69 ua

0.38 ua

REINCUBATE & REMEASURE i's

1.67 ua

0.36 ua

CALCULATIONS

DILUTION FACTOR = 2.1/3.4 = 0.617

RATIOS OF OBSERVED RATES = .224 (.38/1.69) & .216 (.36/1.67)

ASSUMING $RATE_T = k_1[ORG][OX][OH - 0.9]$

WE'D PREDICT A RATIO OF

(.617) (.617) (.617*4.29-0.9)/(4.29-0.9)= 0.196

DILUTION "ORDER"
$[dilution]^n$ = [ratio of reaction rates]

solve for "n" ... get 3.09 & 3.19

EXTRAPOLATION TO SY-101

Hydrogen generation rates from IDA/OXIDANT/BASE mixtures tend to drop with time...quickly at first..but eventually seem to reach definite non-zero "steady state" values. To date, the maximum time that a single batch of reactants has been followed is 160 hours.

That single experiments's steady-state hydrogen production rate corresponded to a current of 0.9 ua from 4.5 millimoles of IDA in 3.5 M free hydroxide, 1.8 M nitrite, and 2.7 M nitrate (run at 95 C with N_2 sparging). If that current is adjusted to reflect SY-101's higher oxidant concentrations (Delegard's estimate was 3.6 M nitrite & 3.9 M nitrate...the same conc. of hydroxide), it grows to about 2.3 ua (0.51 ma/mole of IDA).

There is something like 25 g/l "total organic carbon" in SY-101 and its temperature is said to be about 56 C. 25 g/liter TOC corresponds to an IDA concentration of about 0.5 M. That figure multiplied by the tank's 4.1E6 liter volume gives us 2E6 moles of "organic". If we multiply our experimental 95-degree 0.51 ma/mole figure by 2E6 and then divide it by the approximately 41-fold temperature effect (corresponding to an activation energy of 23 Kcal/mole), we'd predict a current-equivalent continuous hydrogen generation rate of 25 amps in SY-101. That current corresponds to about 1.3E-4 moles of H_2/second (25/(96500 x 2). This is about 7 times less than what it'd take to generate the 7000 ft^3/"burp" hydrogen production rate recently estimated in SY-101.

A relatively modest radiolytic "g factor" for peroxide and/or NO_2 could give the additional chemical reactivity needed to equate IDA expt'l rates with those in SY-101.

CONCLUSIONS

1. Reaction is 1st order in [OXIDANT], [ORGANIC], & [OH - threshold] concentrations.... 3^+ order to dilution...aluminum not important.

2. Especially "active" organics in hot [OX]/[OH] mixtures include glycollic acid, diols, dextrose, & glutaraldehyde. HEDTA is more reactive than is EDTA or IDA. It is unlikely that any of the especially "active" organics originally in feedstock streams still exist in SY-101. Totally non-reactive organics tested include methanol, isoamyl alcohol, acetic acid, benzaldehyde, & benzoic acid. IDA is a reasonable choice of "model" compound.

3. Formaldehyde generates hydrogen quickly and with high yield in hot aqueous base solutions...no oxidant is required. It may be "the" intermediate.

3. Activation energy for overall reaction (IDA) is on the order of 23 kcal/mole (agrees with Delegard's work).

4. Oxidants in order of relative abilities to spur H_2 generation are:
$[NO_{2gas}]>[peroxide]>[O_{2gas}]>[nitrite]>[nitrate]$
(The bottom of SY-101 likely gets some NO_2 & peroxide by radiolysis)

5. Dilution, temperature reduction, & neutralization of excess "free" hydroxide are possible "chemical cures" for SY-101.

ATTACHMENT H

Mechanistic Elucidation of Chemistry in Tank 101-SY

Georgia Institute of Technology

February 7-8, 1991

Professors: Gene Ashby

Kent Barefield

Charles Liotta

Henry Neumann

General Approach (E.C. Ashby)

What is Important, But is Not Known?

1. Accurate rates of reactions
2. Accurate analysis of crust during and after reaction
3. Accurate analysis of gases under various conditions
4. Determination of origin of H_2 and N_2O (^2H and ^{15}N labeling)
5. Analysis of organic products, gases and H_2/N_2O formed during the reaction unde various conditions
6. Effect of radiolysis and calalysis

Descrepencies in Prior Art

1. Agnew - 15% of total gases come from organic compounds in 101-SY

   Delegard - half life (t 1/2) of organic reactions is 100 hours.

2. Delegard - Na AlO_2 necessary for gas evolution

   Siemer - Na AlO_2 not necessary for gas evolution

3. Results from 101-SY $N_2O/H_2 = 0.75$

   Hart - $N_2O/H_2 = 11.7$

4. Delegard - EDTA (thermal rx) does not produce gases

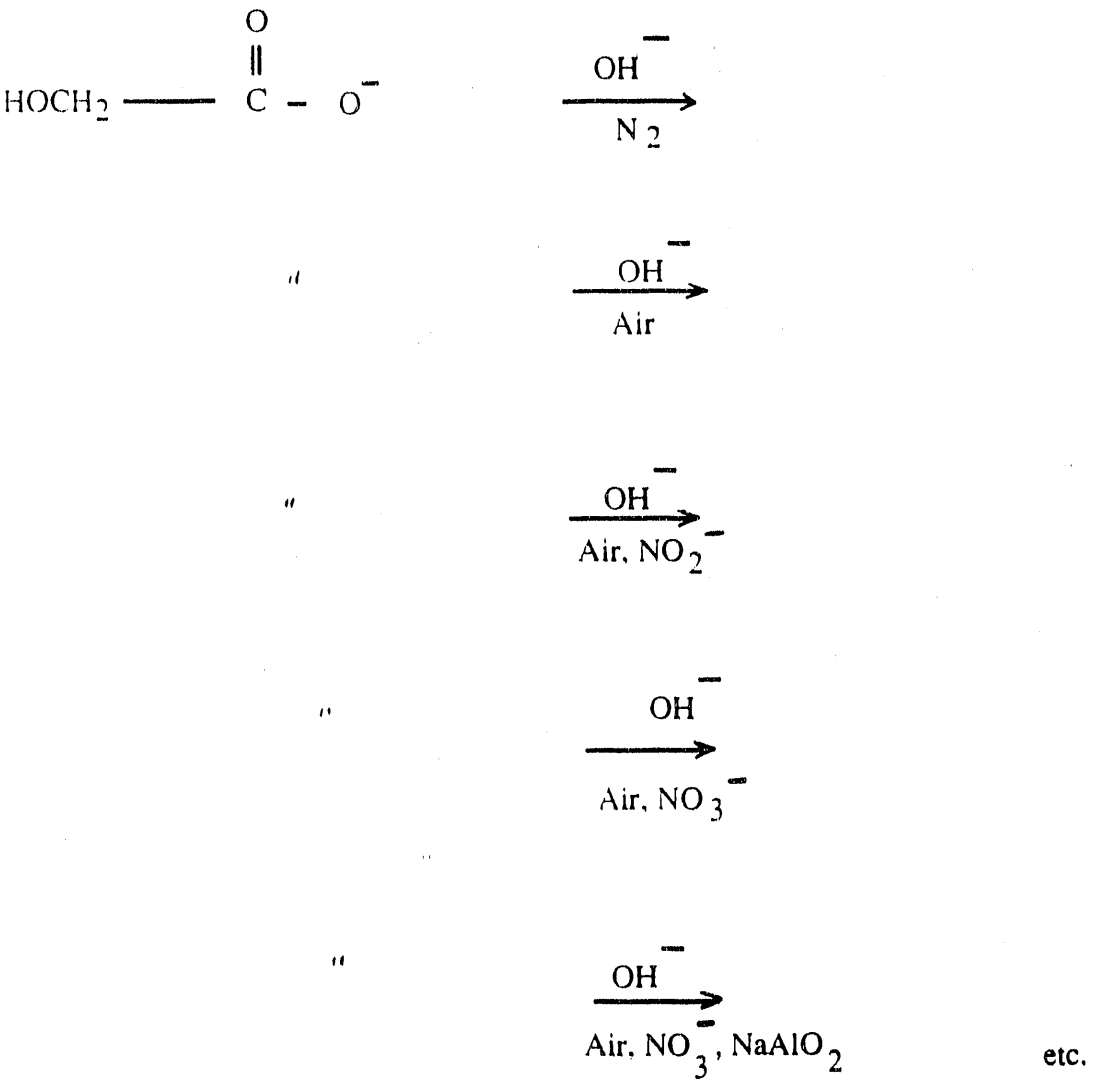
   Hart - EDTA (radiolytic rx.) produces H_2 and N_2O

5. Previous reports - H_2, N_2O, NH_3 are the products gases

   Neumann - N_2 and N_2O are produced in 1:1 ratio

Studies Involving:

(1) Rates of formation of Organic Products:

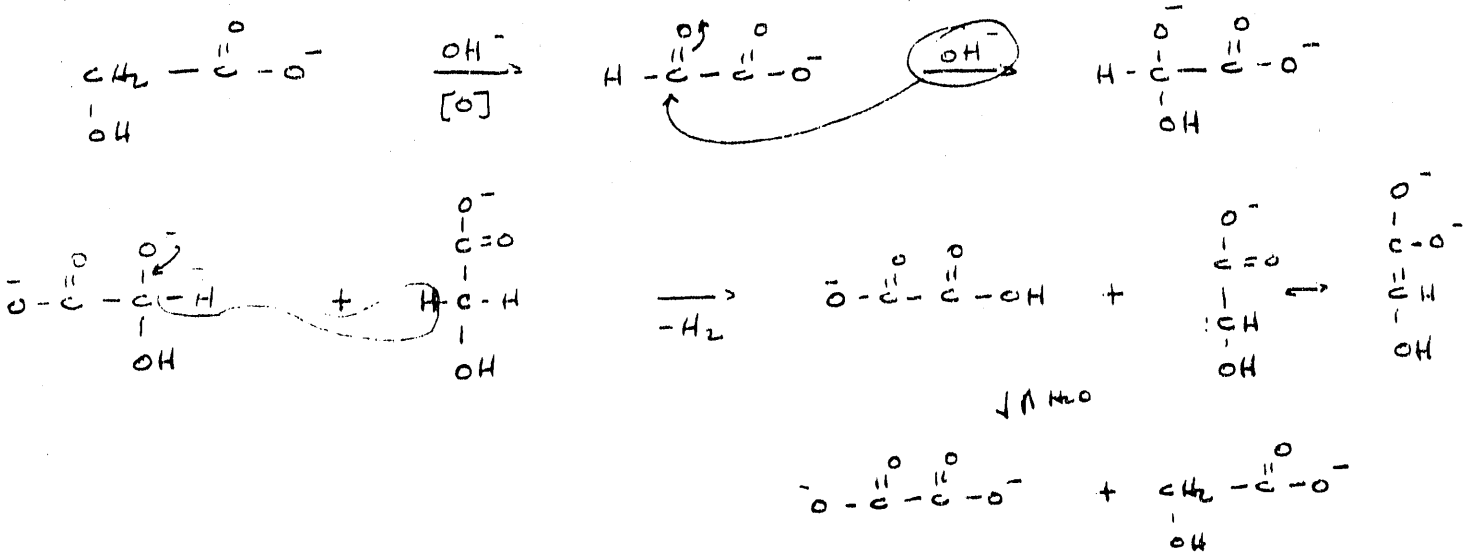


(2) Concentration and stoichiometric studies

(3) Reactions carried out thermally and radiolytically

(4) Analysis of crust at various times during and after the reactions

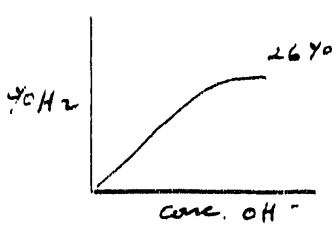
Sterner Results:

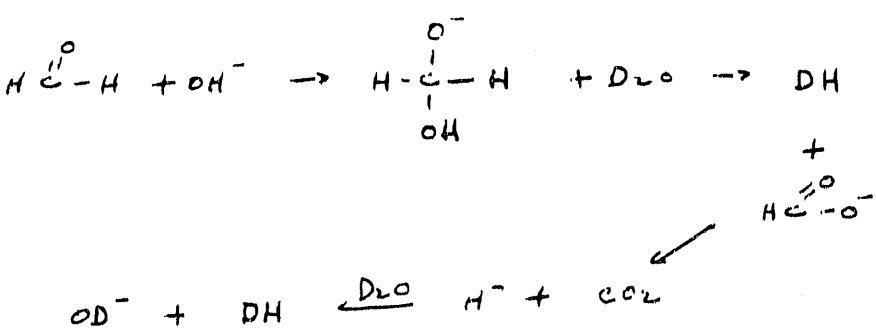


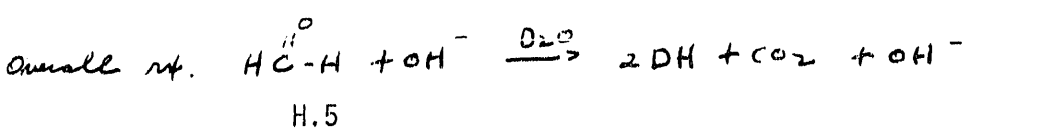
Study reaction quantitatively

(1) determine H_2, oxalate and glycolic acid formed in reaction

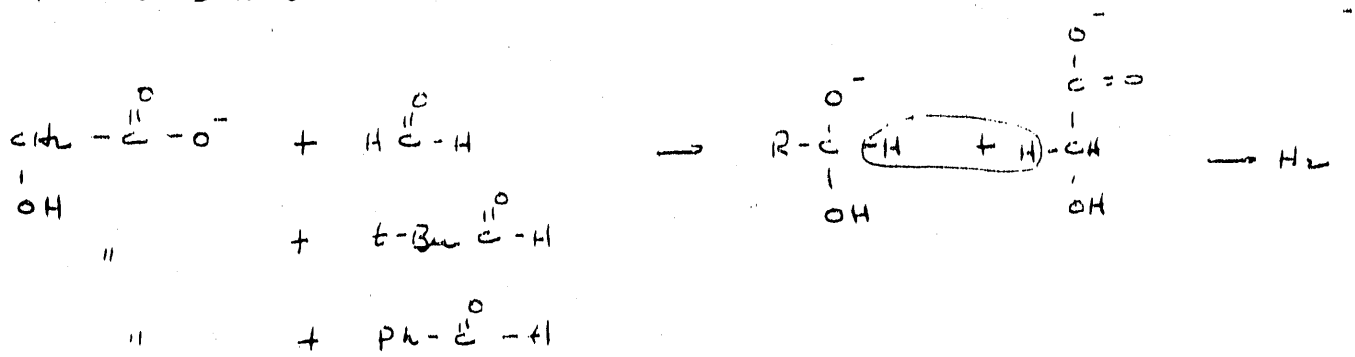
(2) study reaction with formaldehyde







3. Further studies

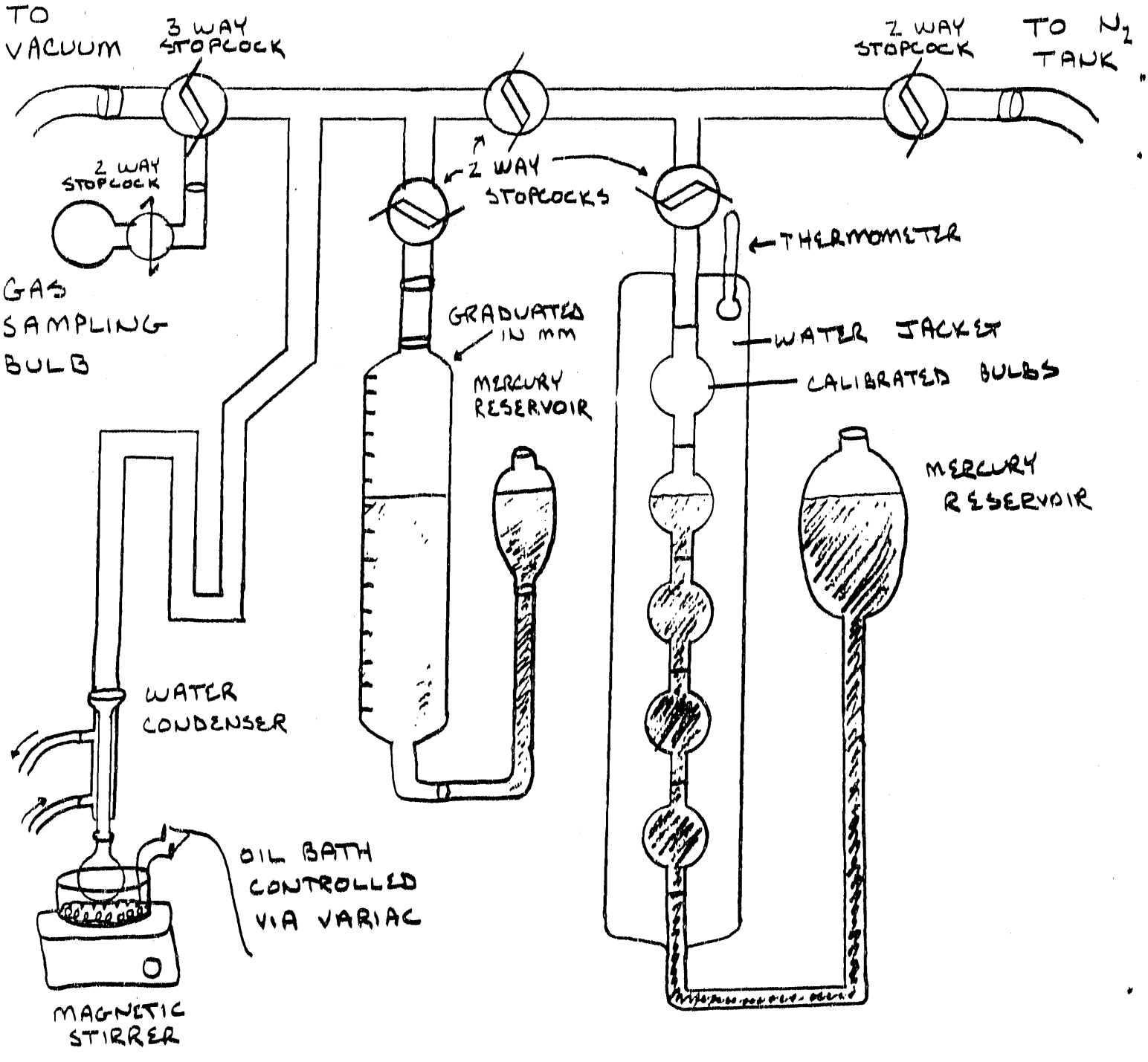


$C_3H_7\overset{O}{\overset{\|}{C}}-H \xrightarrow[{[O]}]{50\%\ NaOH}$ Products (Cannizzaro / alcohol)

KINETICS STUDIES

DR. CHARLES LIOTTA

Initial Kinetic studies to establish integrity of apparatus, concentration of solutions and rates of reaction involving gas evolution.


TO VACUUM
3 WAY STOPCOCK
2 WAY STOPCOCK
TO N_2 TANK
2 WAY STOPCOCK
2 WAY STOPCOCKS
THERMOMETER
GAS SAMPLING BULB
GRADUATED IN MM
MERCURY RESERVOIR
WATER JACKET
CALIBRATED BULBS
MERCURY RESERVOIR
WATER CONDENSER
OIL BATH CONTROLLED VIA VARIAC
MAGNETIC STIRRER

COMPONENTS OF GAS KINETICS
TRIAL A38

COMPOUND	M.W.	[M]	GRAMS
HEDTA	278.96	0.35	9.76
$EDTA \cdot 2Na \cdot 2H_2O$	398.23	0.17	6.77
NaOH	40.00	4.88	19.52
$Na_2O \cdot Al_2O_3 \cdot 3H_2O$	217.99	1.14	24.74
$NaNO_2$	69.00	3.55	24.50
$NaNO_3$	84.99	3.89	33.06
Na_2CO_3	105.99	0.31	3.29

100mL distilled water

TRIAL A 38
AIR ATMOSPHERE

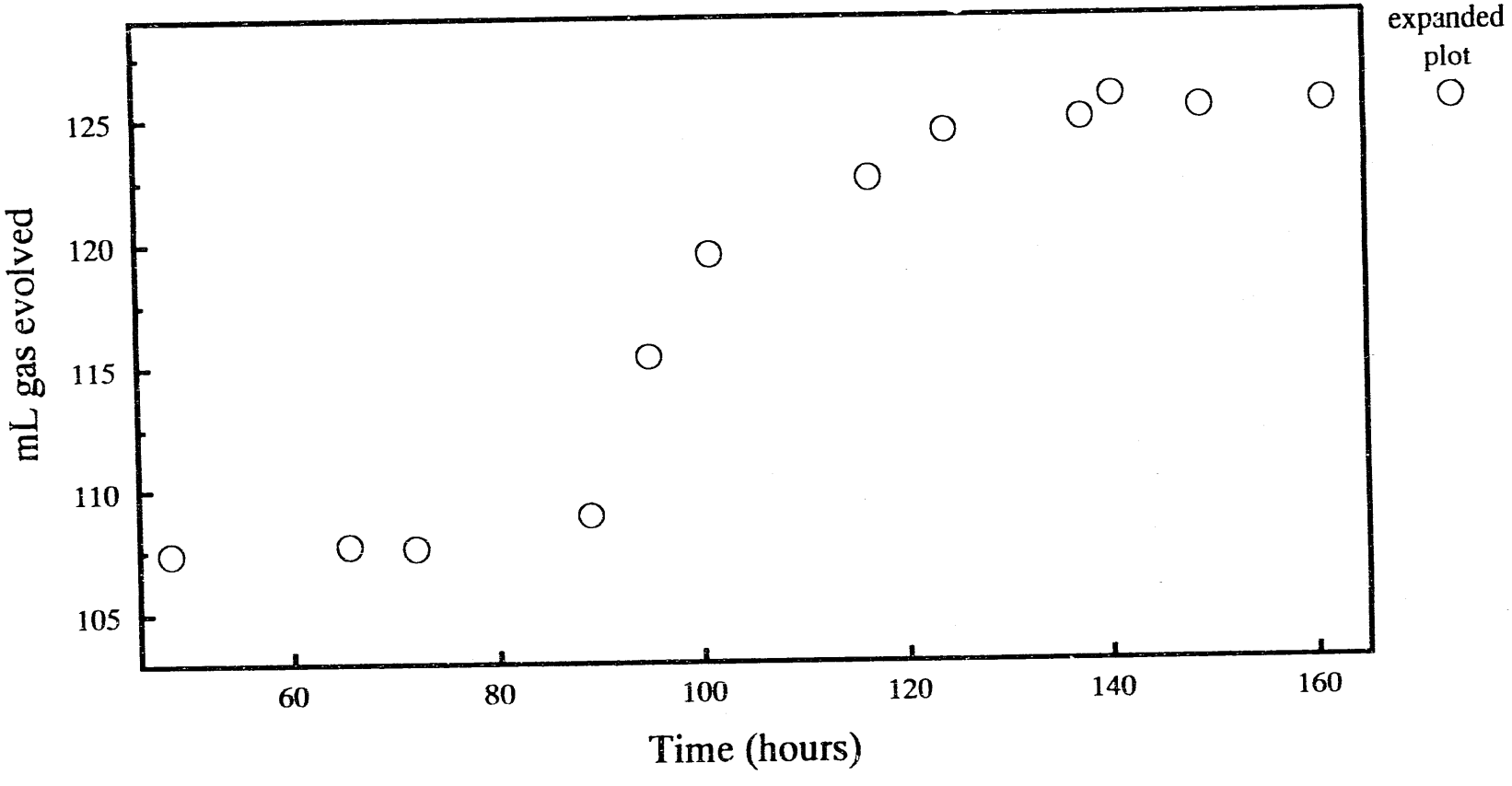
NOT CORRECTED FOR PRESS OR TEMP

Time (hours)	mL gas	oil bath °C	hood °C	barometric press mm Hg
0	0	122	26	737
0.25	28.1	90	26	737
0.50	45.0	107	26	737
0.75	60.8	118	26	737
1	72.1	117	26	737
1.25	80.2	120	26	737
1.75	96	124	26	737
17.5	107	120	26.5	733
24	108.7	122	28	733
28	110.1	123	26.5	733
41.5	108	119	25	744
48	107.4	119	25.5	744
65.5	107.7	118	26	750
72	107.6	117	26	750
89	108.9	121	26	
95	115.4	122	26	
101	119.5	122	27	
116.5	122.5	123	26	
124	124.4	122	27	
137.5	124.9	121	25	745
140.5	125.8	122	25.5	745
149	125.3	120	27	745
161	125.5	121	25	

PLOT OF mL GAS vs TIME

TRIAL A38

(expanded plot)



pseudo homogeneous solution
uncorrected for temperature
and pressure

Determination of Reaction Progress and Products by NMR

Dr. Kent Barefield

By NMR can determine:

(1) rate of product formation

(2) nature of the product

(3) hydrogen exchange phenomena

Exploratory ^{1}H and ^{13}C NMR Studies on a Simulated Waste Mixture

Objective:

To examine ^{1}H spectra in D_2O to avoid interference due to H_2O and to check for exchange of HEDTA C-H with solvent.

To examine feasibility of using ^{13}C for studies of HEDTA decomposition.

Conclusions:

Exchange of carboxymethyl group hydrogens with solvent is complete in less than 24 h at 120° C.

Exchange of other protons is not detectable up to 168 h.

Between 24 and 48 h a new resonance appears in the ^{1}H spectrum at δ 8.3; new resonances are also detectable at δ 2.4 and δ 2.8.

At 168 h the above proton resonances are more intense and a new ^{13}C resonance is detectable at δ 180.4 in addition to those at δ 180.6 and δ 180.8 due to HEDTA due to the carboxyl groups. New, unassigned, resonances at δ 45.5 and δ 54.6 are also present.

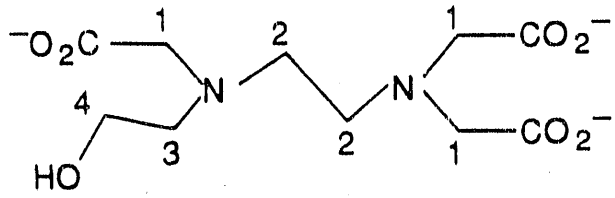
Implications:

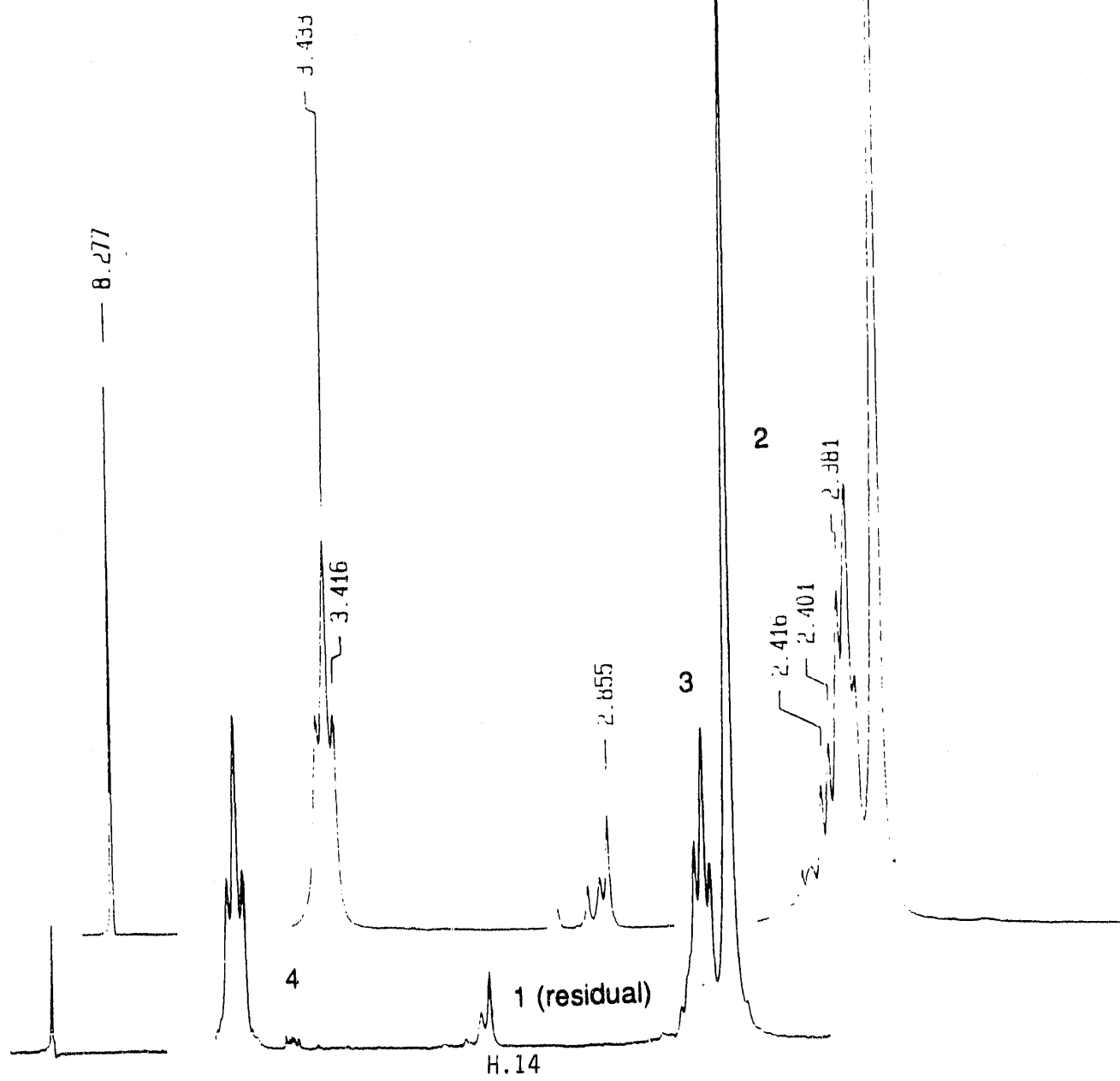
Deuterium labeling of carboxymethyl groups may not be useful in exploring sources of gaseous hydrogen.

NMR should be a useful technique for *in situ* monitoring of the degradation of HEDTA, particularly of ^{13}C labeled materials.

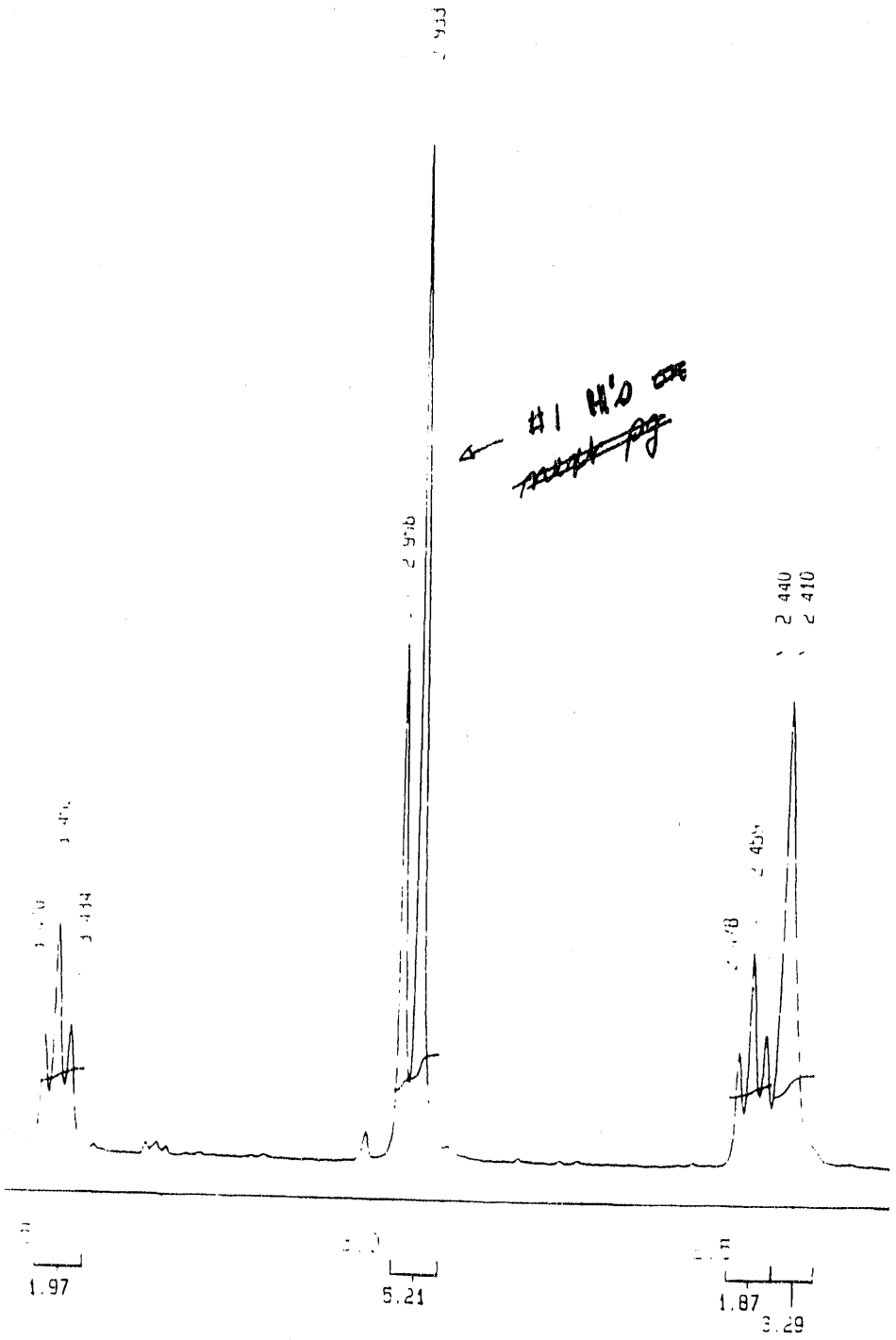
^{1}H NMR spectra at 48 h and 168 h

Solvent – D_2O

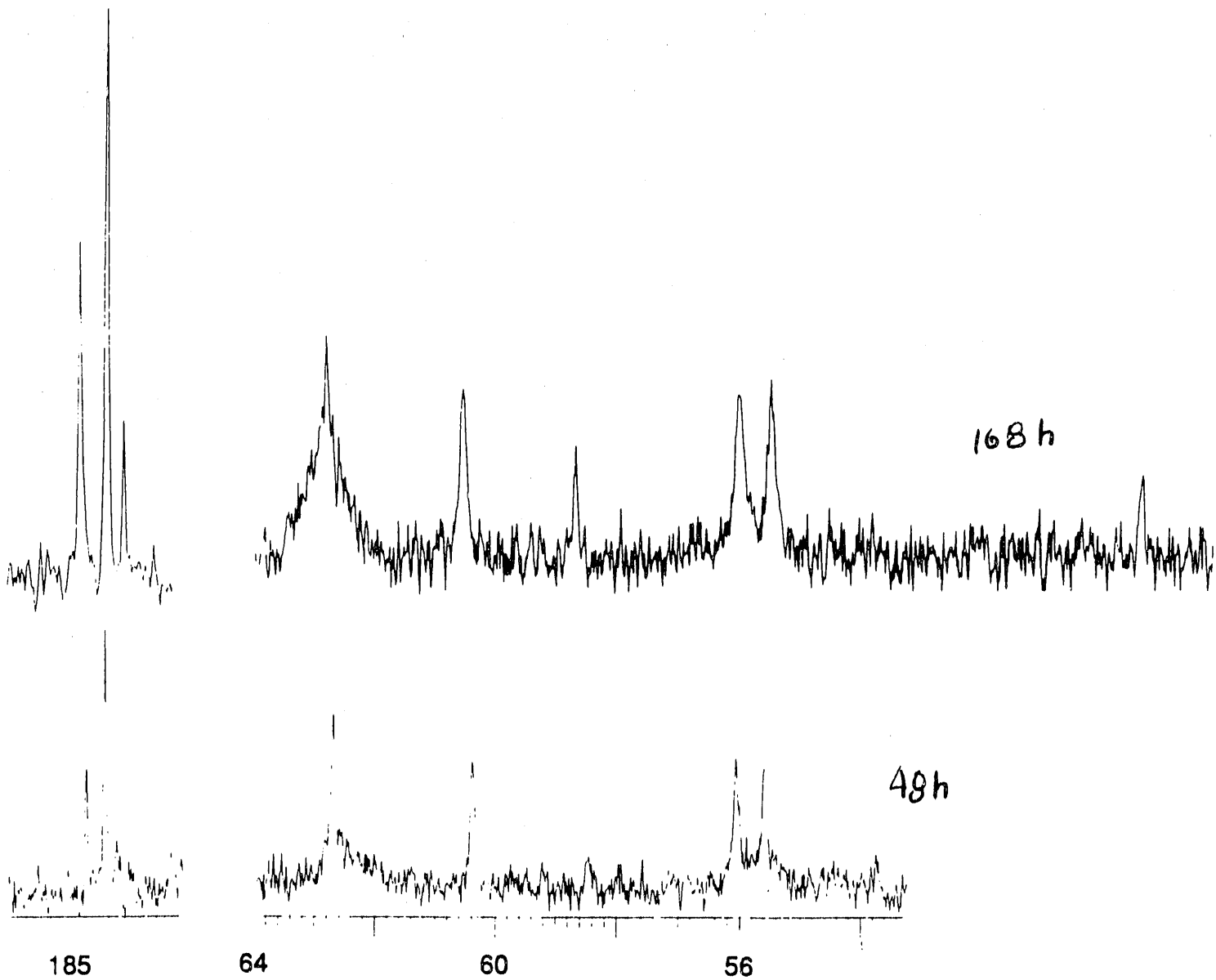




^1H NMR spectrum (D_2O) of HEDTA in basic solution



^{13}C NMR spectra of HEDTA in simulated tank mixture at 48 h and 168 h



Solution Inorganic Chemistry

Thermochemistry

(Dr. Henry Neumann)

Analyses using data from the Delegard, Agnew and Hart reports

Slurries of Delegard Compositions

(1) Compositions of the solid phase (or phases) and of the solution not certain. May vary with order of putting reagents together.

(2) Solution is saturated with at least one of $NaNO_3$, $NaNO_2$, and Na_2CO_3; or any two; or all three.

(3) For systematic study of kinetics, must begin with homogeneous solutions.

Principle oxidizing agent is NO_3

Reduced product could be NO_2, $NO_2^{\cdot}$, N_2O, or N_2 but NO_2 and $NO_2^{\cdot}$ are most commonly observed. In simple mechanisms, 1 electron reducing agents give NO_2, 2 electron reducing agents give $NO_2^{\cdot}$

When NO_2 is formed it would only exist transiently.

NO_2 is known to undergo disproportionation in basic solution

$$2OH^- + 2NO_2 \text{ ------> } NO_2^- + NO_3^- + H_2O$$

Reactions in Table I of Hart report provide a mechanism for this.

31- $NO_2 + NO_2$ ------> N_2O_4	4.6×10^8
32- N_2O_4 ------> $NO_2 + NO_2$	7.0×10^3
27- $H_2O + N_2O_4$ ------> $NO_2^- + NO_3^- + 2H^+$	1.1×10^3
19- $H^+ + OH^-$ ------>H_2O	1.4×10^{11}

In writing a net reaction to account for degradation of a complexing agent, it is assumed that oxidation of C's is due to $NO_3^{\cdot}$ ------> $NO_2^{\cdot}$

Formation of N_2O or N_2 is attributed to reaction of amine nitrogens with $NO_3^{\cdot}$ or $NO_2^{\cdot}$

Estimate of Maximum heat generated

(Agnew Report)

$$EDTA^{4-} + 6NO_3^- + 2NO_2^- + 0_2 \text{ ----> } 6\ CO_3^{2-} + 4CO_2 + 4\ H_2O + 3N_2 + 2H_2 + 2\ N_2O$$

$\Delta H =$
~ -857.3 kcal(-3587 kJ)

$$EDTA^{4-} + 14OH^- + 17NO_3^- \longrightarrow 2N_2O + 2H_2 + 10CO_3^{2-} + 11\ H_2O + 15\ NO_2^-$$

$$\Delta H = -2857\ kJ$$

$$EDTA^{4-} + 14OH^- + 15NO_3^- + 15NO_3^- \longrightarrow 2N_2 + 2H_2 + 10\ CO_3^{2-} + 11\ H_2O + 13\ NO_2^-$$

$$\Delta H = -3221\ kJ$$

$$EDTA^{4-} + 14OH^- + 19NO_3^- \longrightarrow 2N_2O + 10CO_3^{2-} + 13H_2O + 17NO_2^-$$

$$\Delta H = -3227\ kJ$$

$$EDTA^{4-} + 14OH^- + 17NO_3^- \longrightarrow 2N_2 + 10CO_3^{2-} + 13H_2O + 15NO_2^-$$

$$\Delta H = -3591 kJ$$

Conclusion: Estimate is not very senistive to the reactions chosen since the major effect arises because of oxidation of all C to CO_3^{2-}

If oxidation of C's is less extensive, ΔH less negative. For example, if $C_2O_4^{2-}$ is product rather than CO_3^{2-}, add + 1275 kJ to each of values above

($C_2O_4^{2-}$ was chosen since data were available to make the calculation)

Both this analysis of the thermal reaction and the results of the radiation chemistry, point to formation of NO_2^- and CO_3^{2-} and the destruction of NO_3^- in solution. Assuming that the solution in the tank in 1980 was either saturated (or close to saturation) in $NaNO_3$, $NaNO_2$, and Na_2CO_3, the solids coming out of solution now are probably $NaNO_2$ and Na_2CO_3. It is possible that $NaNO_3$, deposited at an earlier time, is now dissolving.

<u>A consideration related to crystallization of Na_2CO_3 from media containing NO_3^-</u>:

Studies of incorporation of foreign ions into a forming crystal lattice indicate that ions of the same size are frequently incorporated: The NO_3^- and CO_3^{2-} ions would be almost identical in size and shape. Thus NO_3^- might occupy sites in the lattice normally occupied by CO_3^{2-}. To maintain electroneutrality, there would be an appropriate number of vacancies at normal Na^+ sites. A crystal with such defects would have a lower density than normal Na_2CO_3. Only a limited amount of these defects could occur without distortion of the crystal lattice.

Comments on Mass Spectrometer Data for October 24, 1990, Gas Release
(Data from Preliminary Results, 241-SY-101 Tank Venting, October 24, 1990; Presented by D. G. Baide)

Has anyone pointed out that the mass spectrometer data strongly suggest that N_2O and N_2 appear in the products in a 1:1 ratio?

In the following it is assumed that the sample being analyzed at any time is a mixture of product gases and air of normal composition. It is further assumed that O_2 is not a product gas. The ratio of N_2/O_2 is 3.913 at the first time measured (0625), and it then decreases to an average value of 3.719 after 1200. The value of 3.719 is taken as characteristic of natural air. Hence the difference between the measured ratio at some time and 3.719 is a measure of the amount of product N_2 in the mixture.

The table shows the ratios of product N_2/O_2 and of N_2O/O_2at various times. The conclusion is that N_2 and N_2O are formed in equal amounts within the accuracy of the data.

This is a surprising result, as one would have expected N_2 and N_2O to be formed by separate mechanistic paths. Some constant ratio would have been expected for product N_2/N_2O if they are formed by separate mechanistic paths, but that the ratio would be 1:1 by coincidence is extremely unlikely. The results suggest that N_2O and N_2 are formed along a single mechanistic path.

Is there some other explanation for these observations?

Time	N_2/O_2	(product N_2)/O_2	N_2O/O_2
0625	3.913	0.194	0.199
0636	3.893	0.174	0.172
0647	3.853	0.134	0.146
0658	3.814	0.095	0.127
0720	3.793	0.074	0.095
0735	3.809	0.090	0.076
0750	3.762	0.043	0.061
0810	3.773	0.054	0.047
0830	3.770	0.051	0.039
0852	3.784	0.065	0.032
0912	3.748	0.029	0.027
0932	3.761	0.042	0.022
0952	3.748	0.029	0.019
1012	3.739	0.020	0.015
1042	3.739	0.020	0.013
1132	3.745	0.026	0.007

1232	3.718	Average = 3.719
1332	3.712	
1431	3.732	
2001	3.714	
0449	3.719	

ATTACHMENT I

OBSERVED RESULTS FROM RADIOLYSIS IN AN SRS WASTE TANK
(DATA TAKEN IN 1974)
NED E. BIBLER

SOLUTE CHANGES:

NITRITE INCREASES, NITRATE DECREASES

GAS EVOLUTION:

EXPERMENTAL MIXTURE:

N_2	36.8%
O_2	56.4%
H_2	7.5%

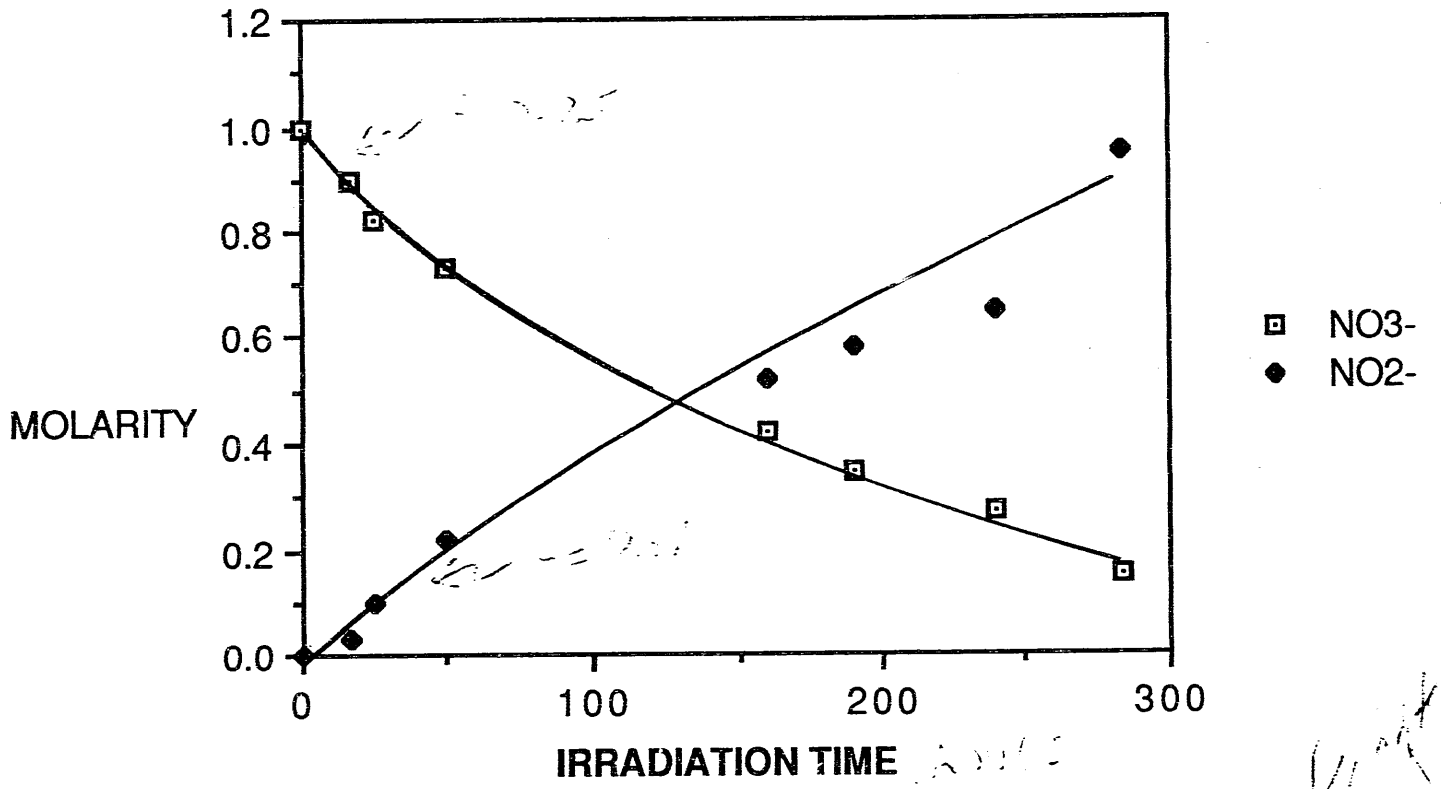
COMPOSITION AFTER AIR REMOVAL:

O_2	86%
H_2	14%

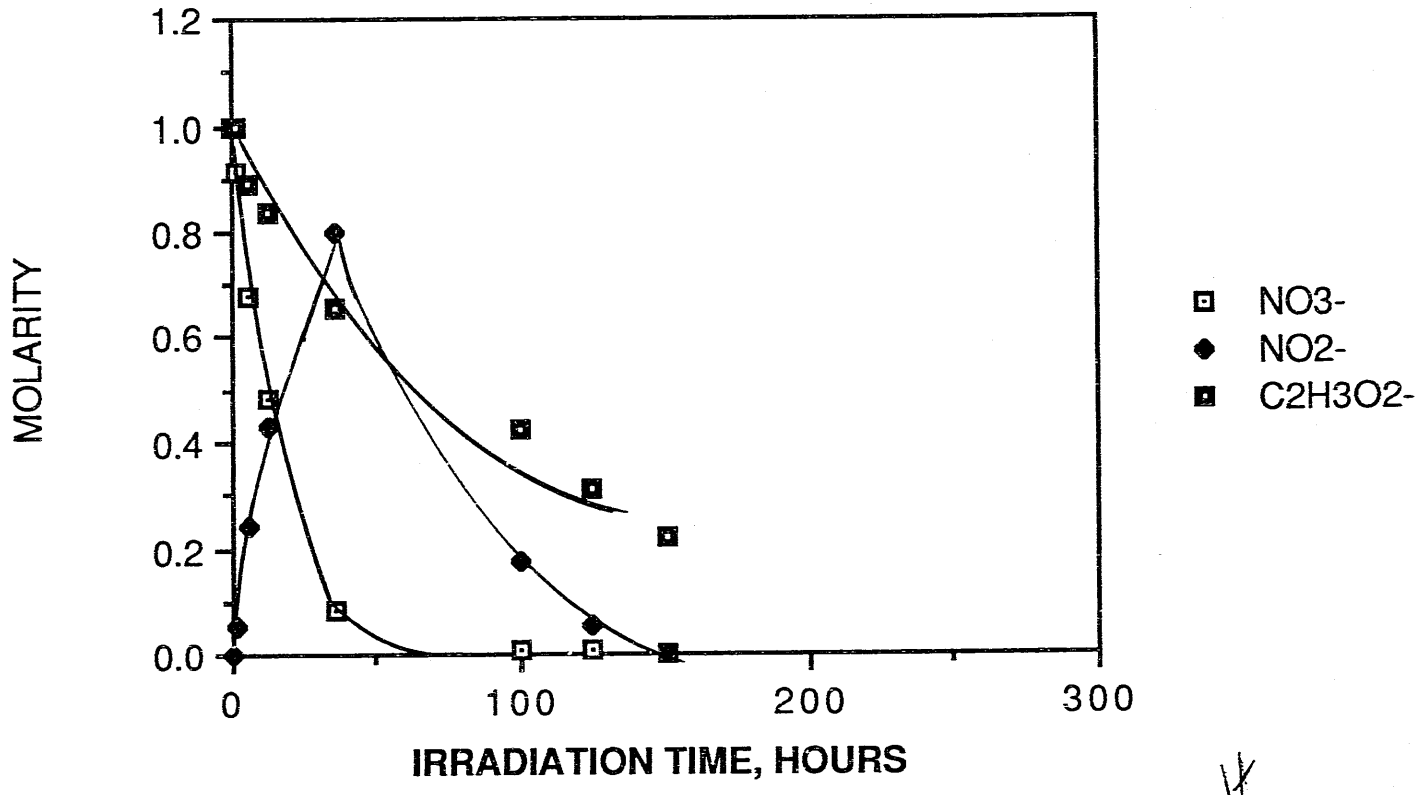
$O_2/H_2 = 6.1$

THIS IS REASONABLE FOR A 3-4 M NO_3^- SOLUTION

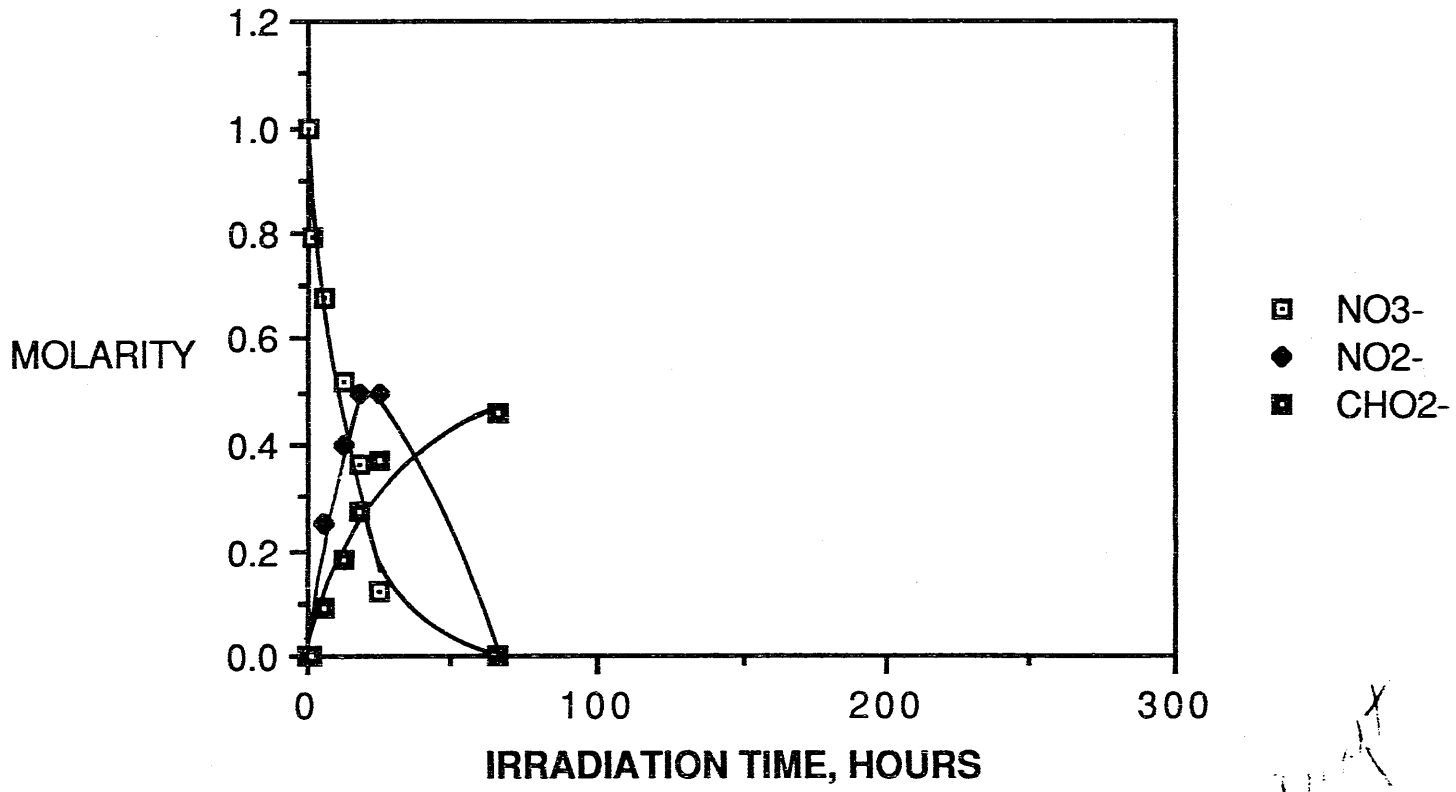
RADIOLYSIS OF NEUTRAL NITRATE SOLUTIONS



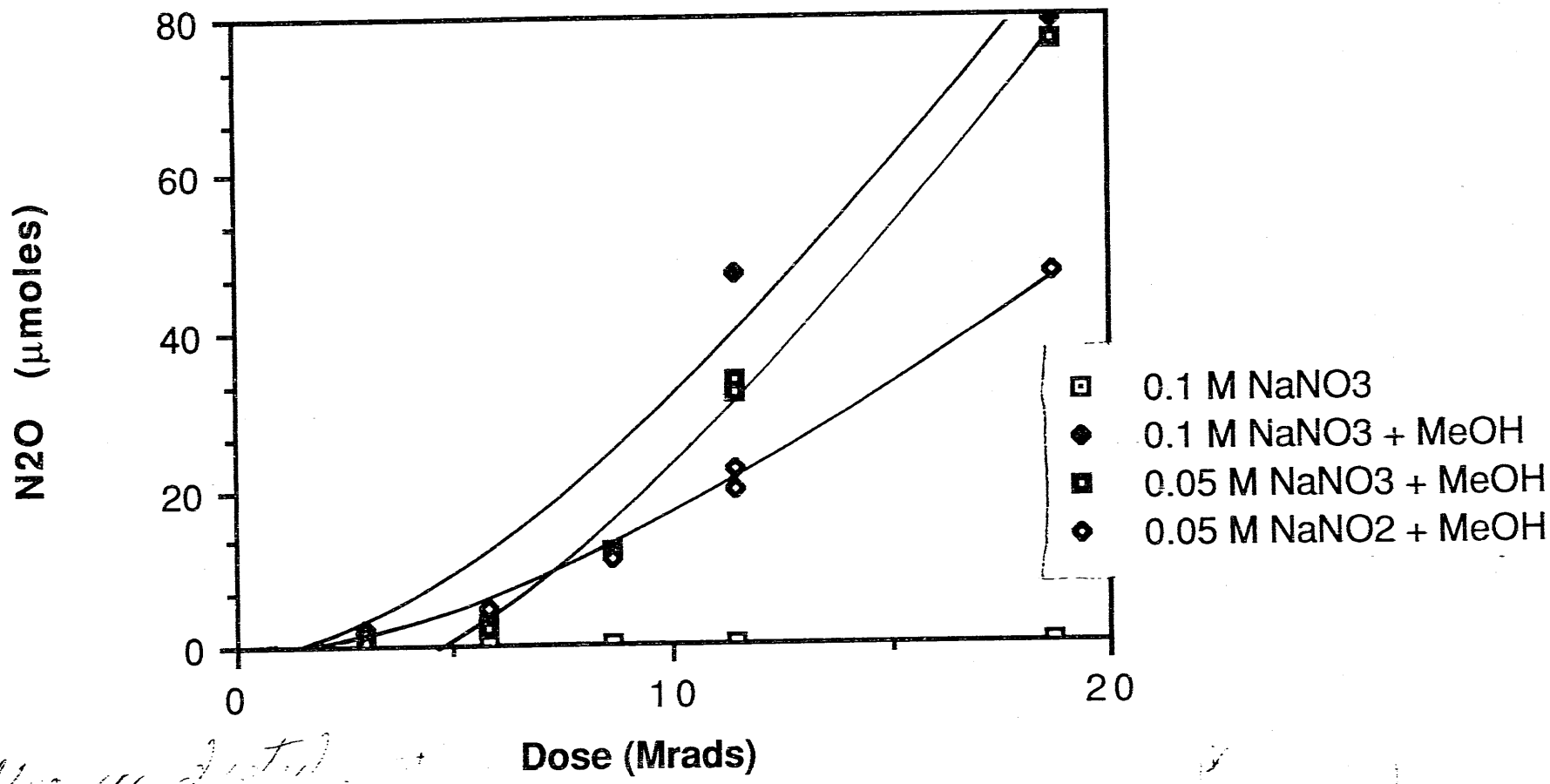
RADIOLYSIS OF NITRATE-ACETATE SOLUTIONS



NITRATE-ETHYLENE GLYCOL (1M) SOLUTIONS



Irradiation of 0.10 M MeOH Solutions



ATTACHMENT J

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

Telephone: 708-972-3472
FAX Number: 708-972-4993

February 11, 1991

Dr. Thomas H. Dunning, Jr.
Molecular Science Research Center
Battelle Pacific Northwest Laboratories
Richland, Washington 99352

Dear Tom:

Phil Horwitz requested that I send you copies of the transparencies that I used in my short presentation to the Tank Science Panel. These are enclosed here. Obviously, they were part of a presentation, but if you need further clarifications, I will be happy to provide them to you. I found the meeting enlightening.

With best regards,

Sincerely yours,

Dan Meisel

Dan Meisel
Chemistry Division

DM/lb

encl.

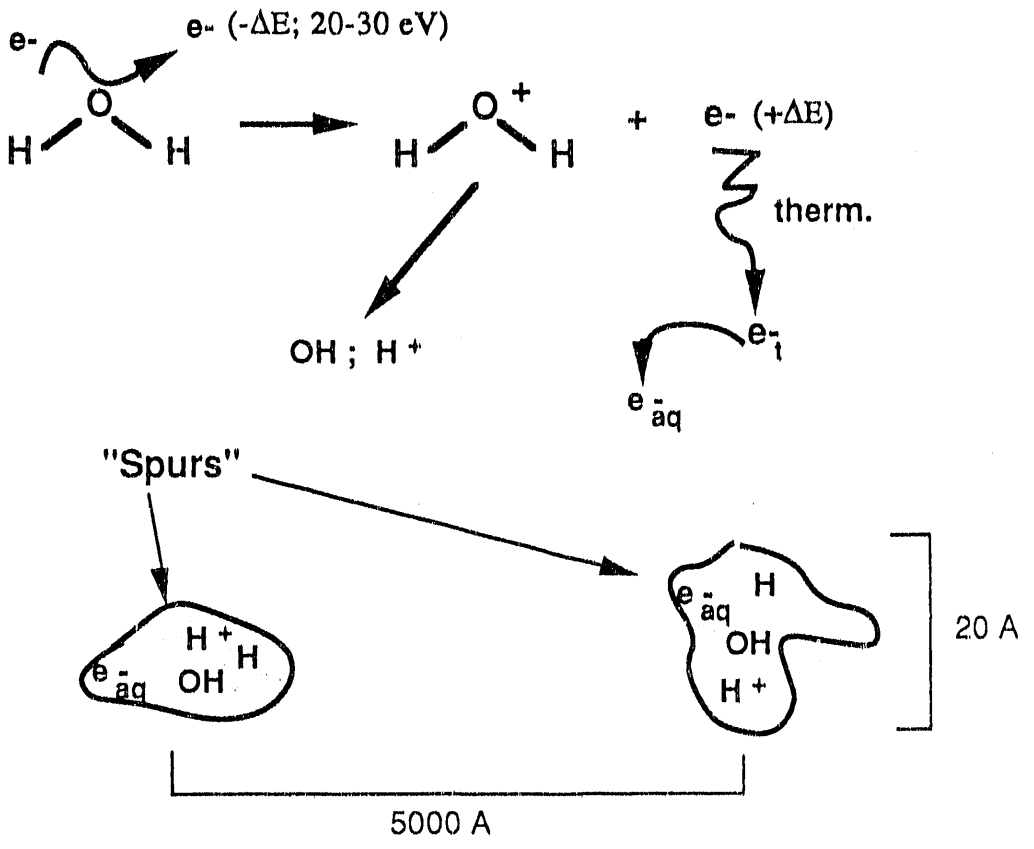
(γ or β Radiation)

$$H_2O \rightsquigarrow e^-_{aq} ; H^\bullet ; H_2 \qquad OH ; H_2O_2; \qquad H^+$$

$$e^-_{aq} + NO_3^- \xrightarrow{H_2O} NO_2 + 2OH^- \quad (k=1.0\times10^{10}\ M^{-1}s^{-1};\ \text{in 2M nitrate}\ \tau \approx 35\ \text{ps})$$

$$OH + NO_2^- \rightarrow NO_2 + OH^- \quad (k=1.0\times10^{10}\ M^{-1}s^{-1};\ \text{in 2M nitrite}\ \tau \approx 35\ \text{ps})$$

Early Stages



Consequences:

1. Fast ($<10^{-12}$ s)
   a. "Direct" Effects (>22% of the energy is absorbed by NO_3^- at 5M)
   b. Precursors (presolvation) reactions (at 0.5M only 37% e^- solvate)
   c. High base, NO_3^-, NO_2^-, very important to minimize H generation

2. Inhomogeneous kinetics:
   a. Local high concentrations
   b. Competition between: recombination, diffusion and scavenging

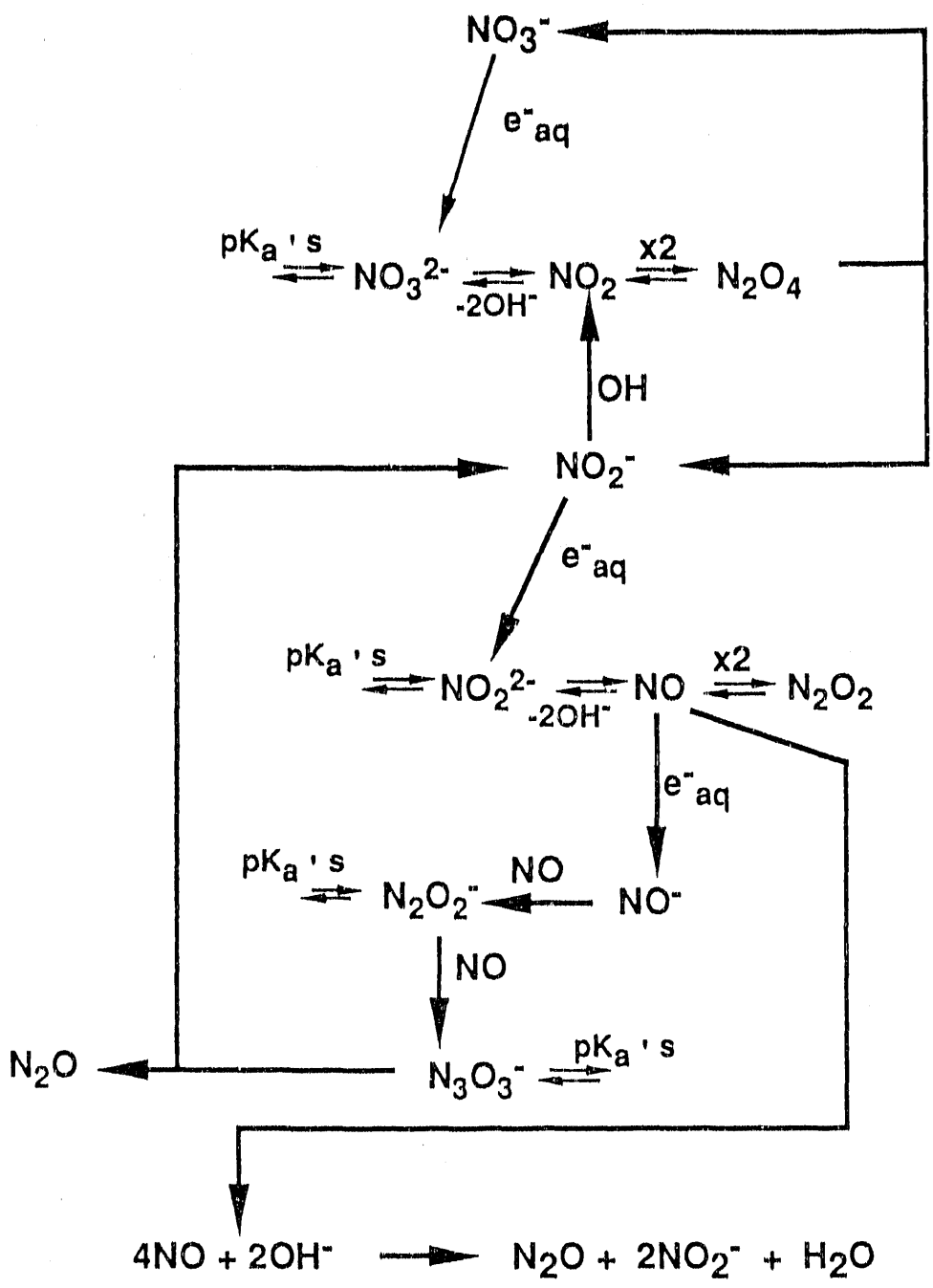
Questions and Answers:

Q. Any H_2 produced directly (Unscavengable) by radiolysis of water? Important because it may be unavoidable.
A. If any, $g_{H_2} \leq 0.06$

Q. Any H produced directly by radiolysis?
A. Definitly; At least with $G_H = 0.65$; but obviously scavengable. We suspect this to be a major concern

Q. Any effect of organics?
A. $H + RH \rightarrow H_2 + R^\bullet$ may be important in either homogeneous ($>10^{-8}$ s) or more probably "spur" competition.

Radiation Chemistry of NO_x



Strategy:

1. What is known already

   Yields; Rate constants; Early effects

2. Establish the facts on simulated wastes

   a. Measure effect of organics on H_2 and N_2O yields (gas chromatogrphy and mass spectrometry). Oxidizing eq. seem of interest only for or $R^{\bullet}$ production.

   b. Measure effects of temperature

   c. Measure effects of high particulates concentrations

3. Model inhomogeneous kinetics of highly concentrated solutions (incl. effects of: Precursors, Viscosity, Ionic strength, Time dependence of k)

4. Offer and test remedies if possible.

ATTACHMENT K

SUMMARY OF RISO RESULTS

SOLUTIONS USED: 1.56M NaOH; 1.0M $NaAlO_2$; 1.5M $NaNO_3$; 1.5M $NaNO_2$; 0.025M EDTA; 0.025M Citric Acid.

In EDTA solutions $G(H_2) = 0.013$; $G(N_2O) =).15$; $G(CO_2) = 1.87$ (in the absence of $NaNO_2$). O_2, N_2, N_2O and H_2O_2 were not found in the irradiated matrix.

The reaction mechanism of Table I was run using CHEMSIMUL, the Danish computer program, on the matrix alone with $G(H_2) = 0.06$. Some results are:

H_2 is not consumed by reaction 12.
$G(H_2)$ forms with a yield $G(H_2) = 0.06$.
$G(-NO_3^-) = G(NO_2^-) = 1.57$

Steady state concentrations of the transient species are:

NO_2, NO, O_2	E-09 - E-10 molar
NO_3^{--}; NO_2^{--} N_2O_3; N_2O_4	E-14 "
O^-; e-aq; O_2^-	E-18 - E-22 "

The EDTA and NO_2 free radicals were identified as transient species by pulse radiolysis.

N_2O is 1/30th as soluble in the waste solution as in water.

Flowing an air-8% CO_2 mixture over the waste solution heated to 50 C. produces a crust within 24 hours.

Flowing moist CO_2-free air over the solution for days produced no crust and no noticeable loss of water.

G(OH) = 2.9
G(E[-]) = 4.76
G(H2) = 0.06
G(H2O2) = 0.54
G(H[+]) = 3.86
G(H2O) = -8.74
G(NO2[-]) = 0.3
G(NO3[-]) = -1.2
G(NO2) = 0.9

APPENDIX B

(Time in seconds; Concentrations in moles/liter)

3

NEW start concentrations

CON(H2O) = 40.28
CON(OH[-]) = 2.88
CON(H[+]) = 3.655D-15
CON(NO3[-]) = 3.72
CON(NO2[-]) = 2.96
CON(B) = 10.0
Total Dose..... = 5.66E+04 / 2 yrs 2.83×10^4 /rads
Radiation time per radiation..... = 6.30E+07 2 yrs.
Date of computation:19-OCT-1990, 12:51:46

RESULT TABLE 2.14 s / integration

	TIME	OH	OH[-]	O[-]	H2O	E[-]
19 50	0.00E+00	0.00E+00	2.88E+00	0.00E+00	4.03E+01	0.00E+00
51	3.15E+07	7.21E-20	2.88E+00	2.50E-18	4.03E+01	9.26E-20
52	6.30E+07	7.20E-20	2.88E+00	2.45E-18	4.02E+01	9.31E-20

RESULT TABLE

	TIME	H2	O2[-]	HO2[-]	O2	O2[--]
50	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
51	3.15E+07	1.75E-03	9.51E-23	3.15E-09	8.72E-11	1.39E-36
52	6.30E+07	3.47E-03	1.84E-22	3.15E-09	1.73E-10	1.35E-36

RESULT TABLE

	TIME	O3[--]	H	H2O2	H[+]	O[--]
50	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.64E-15	0.00E+00
51	3.15E+07	0.00E+00	1.39E-05	5.04E-12	2.54E-15	6.71E-19
52	6.30E+07	0.00E+00	5.45E-05	5.05E-12	2.54E-15	6.72E-19

Total Dose..... = 5.66E+04

RESULT TABLE

TIME	OH	OH[-]	O[-]	H2O	E[-]
0.00E+00	7.20E-20	2.88E+00	2.45E-18	4.02E+01	9.31E-20
3.15E+07	7.19E-20	2.88E+00	2.41E-18	4.02E+01	9.37E-20
6.30E+07	7.18E-20	2.88E+00	2.38E-18	4.02E+01	9.42E-20

RESULT TABLE

TIME	H2	O2[-]	HO2[-]	O2	O2[--]
0.00E+00	3.47E-03	1.84E-22	3.15E-09	1.73E-10	1.35E-36
3.15E+07	5.17E-03	2.68E-22	3.16E-09	2.58E-10	1.30E-36
6.30E+07	6.84E-03	3.47E-22	3.17E-09	3.41E-10	1.27E-36

RESULT TABLE

TIME	O3[--]	H	H2O2	H[+]	O[--]
0.00E+00	0.00E+00	5.45E-05	5.05E-12	2.54E-15	6.72E-19
3.15E+07	0.00E+00	1.21E-04	5.06E-12	2.54E-15	6.72E-19
6.30E+07	0.00E+00	2.11E-04	5.07E-12	2.53E-15	6.73E-19

RESULT TABLE

TIME	NO2[-]	NO2	NO3[-]	NO3[--]	NO2[--]
0.00E+00	3.06E+00	2.67E-09	3.62E+00	8.13E-14	2.90E-14
3.15E+07	3.11E+00	2.65E-09	3.57E+00	8.07E-14	2.97E-14
6.30E+07	3.16E+00	2.64E-09	3.52E+00	8.01E-14	3.04E-14

RESULT TABLE

TIME	NO	N2O4	N2O3	O	B
0.00E+00	8.09E-10	6.38E-14	5.48E-14	0.00E+00	9.97E+00
3.15E+07	8.32E-10	6.33E-14	5.61E-14	0.00E+00	9.95E+00
6.30E+07	8.54E-10	6.27E-14	5.73E-14	0.00E+00	9.94E+00

RESULT TABLE

TIME	P	HEAT	TEMP
0.00E+00	3.17E-02	0.00E+00	3.00E+02
3.15E+07	4.76E-02	0.00E+00	3.00E+02
6.30E+07	6.34E-02	0.00E+00	3.00E+02

12

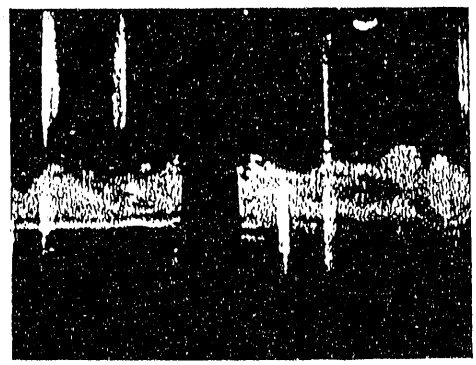


PHOTO I (SIDE VIEW)

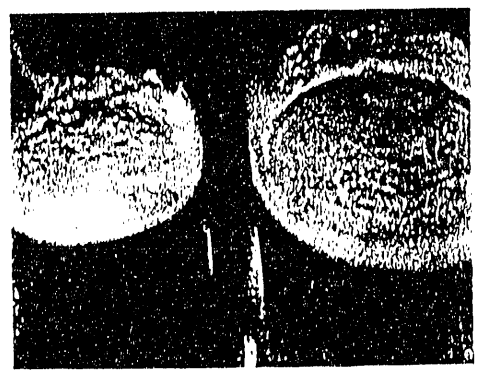


PHOTO II (TOP VIEW)

Fig. 7. Sodium Carbonate Crust Formed on Waste-Type Solutions by the Flow of an Air-0% CO_2 Mixture. (See text for composition of solutions and discussion of results).

ANALYTICAL CHEMISTRY LABORATORY
Report of Analytical Results
ACL Job. No. 91-0113-01 through -12

	# 1	# 2	# 3
	0.175 CA 1674	# 11 A/4 4093	A/4 389.6
H_2	3.21 ± 0.05	32.5 ± 0.3	1.36 ± 0.02
He	82.8 ± 0.3	40.7 ± 0.4	84.8 ± 0.3
H_2O	0.014 ± 0.007	3.8 ± 0.4	0.04 ± 0.01
N_2	9.55 ± 0.10	6.7 ± 0.1	6.34 ± 0.07
O_2	2.10 ± 0.02	16.0 ± 0.2	7.28 ± 0.07
Ar	0.12 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
N_2O	2.15 ± 0.11	0.25 ± 0.05	0.064 ± 0.004

	# 4	# 6	# 7	
	A/4 2772	0.085 EDTA 3122	A/4 389.6	Gas .644
H_2	6.9 ± 0.1	1.72 ± 0.03	2.5 ± 0.3	3.6
He	0.003 ± 0.001	0.14 ± 0.01	42.0 ± 2.1	
H_2O	3.8 ± 0.4	0.64 ± 0.06	~~30.6 ± 3.0~~	
N_2	73.7 ± 0.7	66.4 ± 0.7	13.7 ± 0.7	19.7
O_2	14.5 ± 0.2	16.9 ± 0.2	10.9 ± 0.5	15.7
Ar	0.90 ± 0.02	0.78 ± 0.01	0.16 ± 0.02	
N_2O	0.13 ± 0.04	13.5 ± 0.7	0.09 ± 0.03	0.14

	# 8		# 9	# 10
	0.175 HEDTA 1497	Gas .72	0.175 GA 1664	0.175 HEDTA 3122
H_2	11.9 ± 0.6	16.5	5.3 ± 0.1	4.5 ± 0.1
He	0.31 ± 0.03		76.5 ± 0.7	0.026 ± 0.002
H_2O	28.0 ± 2.8		3.4 ± 0.4	3.0 ± 0.3
N_2	14.1 ± 0.7	19.6	7.3 ± 0.1	58.9 ± 0.6
O_2	0.67 ± 0.03	0.93	0.92 ± 0.02	12.8 ± 0.2
Ar	0.05 ± 0.01		0.09 ± 0.01	0.66 ± 0.07
N_2O	44.9 ± 2.7	62.4	6.5 ± 0.4	20.1 ± 1.0

ALL SAMPLES SHOW H2 AND N2O
A/4 (MATRIX); H2 MUCH GREATER THAN N2O
A/4'S LIBERATE O2
EDTA AND HEDTA; N2O MUCH GREATER THAN H2

HIGH He DILUTION IN 1, 3, 7, 9 AND 11
HIGH H2O IN 7 AND 8
HIGH AIR IN 4, 6 AND 10

SUMMARY OF ANL MASS SPECTROMETR ANALYSES

MATRIX = 2.27 M $NaAlO_2$; 3.49 M NaOH; 3.55 M $NaNO_2$; 3.89 M $NaNO_3$.
This mixture was heterogenous and was dilited by factors of 2 (M/2) and 4 (M/4).

FEATURE	DOSE KRAD	DENSITY G/CC	MASS SPECTRA Y(H_2)	Y(N_2O)	GAS CHROMATOGRAPHY Y(H_2)	Y(N_2O)
M/4	389.6	1.143	0.089	0.004		
M/4	2772	1.143	0.017	0.0003	0.012	
M/4	4093	1.143	0.085	0.0006		
M/2+0.175M CA	1678	1.294	0.035	0.024	0.047	
M/2+0.175M GA	1669	1.287	0.045	0.055		
M/2+0.085M EDTA	3122	1.284	0.0018	0.014		
M/2+0.175M HEDTA	3122	1.286	0.0265	0.110	0.02	0.182

Yield (Y) in microM/l. G(X) = 0.964 x Y(X)

SUMMARY OF ANL GAS CHROMATOGRAPHY ANALYSES

SOLUTION IN M/2	DOSE	DENSITY	Y(H_2)	Y(N_2O)
0.0425 EDTA+0.0875 HEDTA	75.1	1.285	0.044	0.38
"	3097	1.285		0.98
"	131.9	1.285		0.56
0.085EDTA+0.175HEDTA	282.8	1.280	0.088	
0.085 EDTA	131.9	1.284		1.09
0.175 HEDTA	131.9	1.286		0.38
NO $NaAlO_2$	2972	1.233		0.0016
EDTA+HEDTA(conc)	305.0	1.391	0.099	
"	1698	1.391		0.695

WHERE DOES THE EXTRA HYDROGEN COME FROM?

101-SY RESULTS SHOW THAT THE N2O/H2 RATIO IS ABOUT 1.0.

CO-60 GAMMA RAYS SHOW AN N2O/H2 RATIO OF ABOUT 10.

AUGUST BURP SHOWS A RATIO OF 0.75 AT A GAS VOL OF 7000 CUBIC FT.

7000 FT CUBIC FT EQUALS	64.0	CUBIC FT/DAY
G(H2) = 0.06 PROVIDES	13.3	"
H2 NEEDED FOR 0.75 RATIO	42.3	"
H2 UNACCOUNTED FOR	29.0	"

RADIATION PRODUCED H2 HAS TWO SOURCES (1) SPUR AND (2) SCAVENGING OF H-ATOMS BY ORGANIC MOLECULES.

THE MECHANISM:

SPUR REACTIONS	k(M-1s-1)
H + H --> H2	1.0 E+10
H + NO3- --> NO2 + OH-	1.4 E+06
H + NO2- --> NO + OH-	7.1 E+08

If G(H2) = 0.06 for 3.0 M NaNO3, then G(H2) = 0.00012 for 3.0 M NaNO3 + 3.0 M NaNO2.

CONCLUSION: G(H2) = 0.06 IS FAR TOO HIGH FOR 101-SY SOLUTIONS.

REACTIONS IN 0.1 M SCAVENGER	K(M-1s-1)	f(H)	G(H2)
H + EDTA --> H2	6.0 E07	0.0020	0.0007
H + HCOO- --> H2	2.1 E08	0.0096	0.030
H + HPO3-- --> H2	2.0 E09	0.084	0.250

CONCLUSION: RADIATION IS A MINOR SOURCE OF H2 IN EDTA SOLUTIONS

THERMAL STUDIES (26 HOURS AT 80 C)

SOLUTION	VOL(l)	DENSITY	microM N2O	microM N2O/hr.
EDTA + HEDTA (conc)	0.0145	1.391	126.5	4.87
M/2+ 0.175 M CA	0.011	1.284	91.7	3.53
M/2 + 0.175 M CA	0.011	1.294	NONE	---

ESTIMATE OF RATE AT 130 F (54.4 C)

ASSUME AN ACTIVATION ENERGY OF 14400 CAL/MOLE. THEN THE RELATIVE RATE (80 C/54.4 C) = 0.2

THEN THE ESTIMATED THERMAL RATE AT 130 F.IS 0.2 X 4.87 = 0.975 microM N2O/hr.

ASSUME THAT THE RADIATION RATE IS INDEPENDENT OF THE TEMPERATURE.

THEN THE RADIATION RATE IN TANK 101-SY = 0.695 X 3.25 KRAD/hr = 2.26 microM N2O/hr.

FRACTION THERMAL = 0.975/3.235 = 0.30 (30%)

REACTIONS FORMING N2O

HIGH LEVEL WASTES PRODUCE H2, N2O AND CO2 WITH
G(H2) = 0.32, G(N2O) = 0.91 AND G(CO2) = 3.64.

ADDING NH2NH2 GREATLY INCREASES G(N2O AND G(N2)

$N_2H_4 + HNO_2 \rightarrow N_2O + NH_3 + H_2O$

$N_2H_4 + H_2O_2 \rightarrow N_2 + 4\ H_2O$

FORMIC ACID DENITRIFICATION OF WASTES PRODUCES N2O

$HNO_2 + HCOOH \rightarrow HNO_{\cdot} + CO_2 + H_2O$

$HNO_2 + HCOOH \rightarrow NO + HCOO_{\cdot} + H_2O$

$HNO_{\cdot} + NO \rightarrow N_2O + OH_{\cdot}$

THERMAL REACTIONS OF NO

$2KOH + 4NO \rightarrow 2KNO_2 + N_2O + H_2O$

$K_2SO_3 + 2NO \rightarrow K_2SO_4 + N_2O$

PULSE RADIOLYSIS REACTIONS

$N_2O_2^- \rightarrow N_2O + O^-$

$N_3O_3^- \rightarrow N_2O + NO_2^-$

NEW REACTIONS FOR THE MECHANISM OF TABLE I

	k(M-1s-1)
$H_2O \rightarrow H + OH$	
$H + H \rightarrow H_2$	1.0 E10
$H + OH^- \rightarrow E^-_{aq}$	2.0 E07
$OH + OH \rightarrow H_2O_2$	4.0 E09
$NO + O_2^- \rightarrow NO^- + O_2$	1.0 E10
$NO + NO^- \rightarrow N_2O_2^-$	2.5 E09
$N_2O_2^- + NO \rightarrow N_3O_3^-$	4.9 E06
$N_2O_2^- \rightarrow N_2O + O^-$	3.5 E02
$N_3O_3^- \rightarrow N_2O + NO_2^-$	2.5 E02
$H + EDTA \rightarrow H_2 + EDTA_{\cdot}$	6.0 E07
$NO + EDTA_{\cdot} \rightarrow EDTA{:}NO$	FAST
$EDTA{:}NO \rightarrow N_2O + PRODUCTS$	SLOW

ATTACHMENT L

Mr. John L. Deichman,
Manager Waste Tank Safety Program
Westinghouse Hanford Company
PO Box 1970
Richland, WA

Dear John:

SUMMARY OF THE TANK WASTE SCIENCE PANEL MEETING

A meeting of the Tank Waste Science Panel was held in Denver, CO on February 7 & 8, 1991. The purpose of the meeting was to discuss the latest results from Tank 241-SY-101 and from the work that has been carried out both by the Panel members and by those funded to perform studies on the chemical and physical mechanisms taking place in this tank. The purpose of this letter is to provide a brief summary of this meeting; complete meeting minutes will follow.

The meeting started with the sad news that Dick Wallace from Savannah River Laboratory had a massive heart attack on January 18, 1991. N. E. (Ned) Bibler, who will be replacing Dick, indicated that the prognosis is not good. Dick will be missed.

Some of the work that is summarized below has been carried out on the investigator's own time and with existing equipment. Contracts for the studies at Argonne were just recently put in place and the contract for the studies at Georgia Institute of Technology has yet to be completed. For both the work at Argonne National Labs and at Georgia Institute of Technology the process of negotiating the statement of work has substantially delayed the initiation of work. This issue is the subject of a separate letter that will be sent to Westinghouse Hanford Co. management.

Below are bulleted items from the meeting:

- There was a request from one of the Panel member for someone to provide the charters of the other Panels/Task Forces/Committees that are studying this issue and other issues and to provide a statement of where the Tank Waste Science Panel fits into the scheme.

- D. M. (Denis) Strachan presented the results of his attempts at obtaining kinetic information from the waste level data that exist for Tank 101-SY. His analysis suggests that the rate of gas evolution is independent of the physical phenomena taking place in the tank. That is, the gas production occurs all of the time and the burps are the result of the physical phenomena taking place in the tank. Although a more thorough analysis is needed, the data are consistent with the hypothesis that the gas generation rate is a function of the cesium or strontium decay. Also, the gas generation rate appears to be independent of temperature between burps, independent of the hydrogen and other gas pressures, and independent of time between burps. A more formal statistical treatment of the data will be undertaken.

  Denis has also used the tank height data to provide consistency to the model of the crust formation. In the proposed model, the crust is partially formed by waste that is ejected onto the top of the crust during a burp. This model is consistent with the gamma scans, the pictures of the crust, the samples that have been obtained from the crust, and the tank height measurements.

- D. S. (Don) Trent (PNL) presented the results from the numerical

calculation of the October 24, 1990 gas release event. The thermal profile of the waste is similar to that observed. This simulation shows that the process is random and that the flow of the hot waste does not all occur up the side of the tank.

- W. J. (Bill) Thompson (Washington State University) presented the results from a study of synthetic crust provided to him by DL (Dan) Herting and DA (Dan) Reynolds of WHC. The technique used was dynamic x-ray diffraction in which the sample is held in a x-ray diffractometer while it is heated. The heating rate is similar to that used in a differential scanning calorimeter. Gas analyses can also be made. Phase analysis is made at each temperature.

  These results indicate that carbon dioxide is evolved at about 200 C in a nitrogen atmosphere and at about 300 C in air. Nitrogen dioxide and NO are evolved at 300 C in nitrogen and 400 C in air. A correlation between the DSC data and the x-ray diffraction data is still in progress.

- Dan Herting (WHC, invited) presented the results from the chemical and thermal analyses of the samples taken from the crust. This presentation was the same as the presentation made in January 1991 before the High Level Waste Tank Task Force and Technical Advisory Panel.

  Dan presented the results from his gas generation studies. These results indicate a four day induction period, the evolved gases are in different ratios than observed in the tank gases, the reaction rate is independent of the gases evolved, nitrogen is evolved, and oxygen is consumed. His data are consistent with the data obtained by Delegard in 1981.

- Dan Reynolds (WHC) presented data on the October 24, 1990 gas release event. In his presentation, Dan discussed the gamma scans, liquid level detection methods, the status of the waste level measurement systems, the pressure and gas composition during the release event. He also discussed the possibility of diluting the evolved gases by injecting nitrogen at or near the tank bottom. The major engineering problem with this method was delivery of the nitrogen.

- D. D. (Duane) Siemer (WINCO) provided results from his studies on the development of a low level hydrogen sensor. During this development effort, he discovered that hydrogen is evolved from strongly alkaline solutions containing organics. Concentrating on the initial stages of the reaction, he finds no dependence of the generation of hydrogen on the concentration of aluminum, contrary to the results from Delegard. He found that formaldehyde produces hydrogen in the absence of any oxidant. This is the only organic he found that did so; an oxidant was required for all of the other organics studied. The organics he used were selected based on the organics found in the Tank 107-AN waste by Strachan in 1986. He also found the activation energy for hydrogen generation from immidodiacetic acid (IDA) was the same as found by Delegard who started with HEDTA and did not determine the organics remaining in solution after the reaction.

  Duane concluded from the organics he studied that the decomposition reaction is first order in the concentrations of the oxidant, the organic, and hydroxide above some threshold. E. C. (Gene) Ashby (Georgia Institute of Technology) suggested that these results were quite important for the general field of organic chemistry and that the

spin off studies will be of great interest to organic chemists.

- Gene Ashby (Georgia Tech) presented the work that he and his coworkers have done in the absence of a contract. As part of the work they will be doing, they will need organic chemicals with deuterium substituted for hydrogen. They found that several positions are easily exchanged when these organics are in aqueous solution and, hence, no useful information would result from attempting to isotopically label these positions. They developed a synthetic waste solution that can be used as a standard for the waste studies because it is a clear, homogeneous solution, suitable for kinetic studies. The complexity of a slurry can be incorporated later.

  Gene also made some comments on the reactions that had been proposed by Steve Agnew (LANL) and proposed new reactions that were more consistent with the information currently available on Tank 101-SY.

  Gene and his coworkers also looked carefully at the mass spectrometer data from the October 24th event. These data clearly show that nitrogen is being generated and that it is being generated at the same molar amounts as nitrous oxide. The probability of this happening by coincidence is very low. The formation of nitrogen and nitrous oxide in a one-to-one ratio suggests that these originate from a single mechanistic path.

- N. E. (Ned) Bibler (WSRS) talked about the radiochemistry work that has been carried out at the Savannah River Site. From this work, it has been demonstrated that the presence of organics dramatically affects the rate of destruction of nitrate and nitrite and the evolution of hydrogen.

- Dan Meisel (ANL, invited) described some of the theory behind the radiolysis of solution containing high concentrations of nitrate, nitrite, and hydroxide. He did not have results from work performed under contract to WHC since this contract has only been in place for about two weeks. According to the theory, most of the reactions take place in small volumes of solution (spurs) that are about 8 cubic nanometres in volume and separated from each other by about 50 nanometres. Calculations suggest that 22% of the gamma energy is absorbed by the nitrate ion. A series of reactions are possible that yield all of the gases found in the gases released from Tank 101-SY.

- E. J. (Ed) Hart (ANL, retired) discussed the work he performed at the Riso National Laboratory of Denmark while a visiting scientist there. His results indicate that the radiochemistry of typical waste solutions generates more hydrogen than nitrous oxide in the absence of organics and that in the presence of organics, the major gas species is nitrous oxide.

<u>DAY TWO - FEBRUARY 8, 1991</u>

- There was a general discussion of core sampling. There is a general consensus of the panel members that the core sample will not yield all of the information that is needed to develop the physical mechanism. Therefore, there is a need for physical modeling - building and studying small models of the tank and contents - in order to assure the development of a mathematical model of the physical system that will yield credible results and can be used to reliably determine the effect of various remediation schemes. Dan Reynolds, Don Trent, and Bill

Thompson will meet to develop a program based on physical models.

- The role of the Hanford Tank Waste Science Panel was expanded to include the ferrocyanide tanks. There may be a more logical organization of the Science Panel, since not all of the current members of the Panel may wish to deal with the ferrocyanide issues because of expertise or available time. Other issues are sure to follow making a new organizational structure needed. T. H. (Thom) Dunning, Jr. asked the Panel members to submit names of potential Panel members for the ferrocyanide issues.

- L. G. (Larry) Morgan (PNL), Dan Reynolds (WHC), and L. L. (Lee) Burger (PNL, invited) gave the background on the ferrocyanide issues. Dan gave some of the process history and the possible contents of the tanks. Lee presented the work that he has done on the chemistry and characterization of simulated ferrocyanide wastes.

- The Panel was requested by G. D. Johnson (WHC) in a letter to consider three questions. The response to these questions is given below:

  1) The Panel members determined that, based on Dan Herting's results on the recent samples obtained from Tank 101-SY, the potential for the crust to burn is very low.

  2) Although there is still some discussion as to which mechanism is the dominant mechanism for the production of hydrogen, the Panel members agreed that, at this stage of the studies, both thermochemical and radiolytic mechanisms may be used to explain the generation of the gases found in the gases vented from Tank 101-SY.

  3) With respect to increasing the ventilation rate in the tank, the Panel members concluded that the question was too complex to answer at the present time and with the time allotted. The question is outside the expertise of many of the Panel members. Appropriate Panel members will review the Position Paper that will be written by WHC staff.

- Robert Marusich (WHC) set a memo to Denis Strachan requesting assistance on several questions to which he needed information for a safety analysis. The response from the Panel members was that these questions are the same ones the Panel members had raised in June 1990 and represent the scope of work for the Panel.

- Through Larry Morgan, John Deichman (WHC) verbally requested if a gas generation experiment would be useful if additional samples could be obtained while the tank farm crew was obtaining a core sample. The response from the Panel members was to obtain all the samples possible. There will not be enough sample from the core to obtain all of the information needed. This extra sample is needed irrespective of whether a gas generation experiment is performed. In fact, a gas generation experiment may not be high on the priority list, but certainly is a potential use for extra samples.

If you have any question concerning this material, please contact me. Over the next two weeks, I will be writing the more complete version of these minutes.

Sincerely,

Denis Strachan,
Executive Secretary
Tank Waste Science Panel

cc: Tank Waste Science Panel Members
S Agnew (LANL)
LL Burger (PNL)
R Gerton (DOE/RL)
DL Herting (WHC)
BM Johnson, Jr (PNL)
D Meisel (ANL)
GB Melinger (PNL)
LG Morgan (PNL)
JTA Roberts (PNL)
J Tseng (DOE/HQ)
H Walter (DOE/HQ)

ATTACHMENT M

DHK

DRAFT
GL Borsheim
11/5/90

DESCRIPTION OF CESIUM-STRONTIUM SCAVENGING OPERATIONS

The T Plant and B Plant bismuth phosphate process did not recover uranium. The extraction waste, called metal waste, containing the uranium and approximately 90% of the fission products was stored in underground waste tanks. The first decontamination cycle (IC) waste, containing approximately 10% of the fission products was also stored in underground waste tanks.

In order to recover the valuable uranium from the metal waste, the U Plant, built as a third bismuth phosphate plant but not used as such, was converted to a solvent extraction uranium recovery (UR) plant. The metal waste solution was sluiced from the underground tanks, acidified and transferred to the UR plant. The UR plant waste was then returned to underground waste tanks.

The UR process (also called the TBP process since TBP [tributyl phosphate] was the active solvent extractant) began production in November 1952. While the process efficiently recovered uranium from the sluiced, acidified metal waste, the process generated almost two gallons of waste to be stored for every gallon of stored metal waste processed. Ways to reduce the volume of stored waste were studied and resulted in the ferrocyanide scavenging process. (Note that the 242-B and 242-T tank farm evaporators were placed in operation in 1951 to also reduce stored waste volumes.)

The objective of the ferrocyanide scavenging process was to remove the soluble long-lived Cs-137 from the UR waste as a precipitate. The principal other long-lived (approximate 28.5 year half life) fission product, Sr-90, was already essentially insoluble in the neutralized UR waste. The process consisted of adding $Fe(CN)_6^{-4}$ ion to the acid waste, adjusting the waste pH to 9 ±1 and then adding an equal molar amount of Ni^{+2} ion to produce a $Cs_2NiFe(CN)_6$ precipitate and/or carry the cesium down along with other nickel ferrocyanide precipitates such as $Ni_2Fe(CN)_6$. It was not, and still is not

known, what the major ferrocyanide precipitate was. Since the major metal ion in the waste was sodium, the likely major precipitate is $Na_2NiFe(CN)_6$.

The ferrocyanide scavenging flowsheet was tested in U Plant in October 1953. Both ferrocyanide (as $K_4Fe(CN)_6$) and nickel (as $NiSO_4$) were added to 0.005 M in the treated waste. The treated waste (530,000 gallons) was routed to tank T-101 for settling. Control of pH during the first half of the plant test was poor, so only approximately 1/2 (255,000 gallons) of the settled supernate was cribbed in December 1953.[1]

Production scavenging of the UR recovery wastes began in late September 1954. By this time there was a total of approximately 21.2 millon gallons of unscavenged UR waste in the tank farms. (Approximately 13.1 million gallons in 200E Area and approximately 7.9 million gallons in 200W Area.)[2]
The initial production flowsheet consisted of adding 0.005 M $K_4Fe(CN)_6$ to the acid waste and 0.005 M $NiSO_4$ to the waste after pH adjustment to 9 ±1. In some campaigns the pH adjusted waste was partially concentrated before adding the $NiSO_4$.

Flowsheet changes made to the scavenging operation included:[1]

1. Replacing $K_4Fe(CN)_6$ with $Na_4Fe(CN)_6$ (April 18, 1955).

2. Testing and routine addition of $Ca(NO_3)_2$ (0.016M) to improve Sr decontamination (April 21, 1955).

3. Testing and addition of $Sr(NO_3)_2$ (0.004M) to replace $Ca(NO_3)_2$ for Sr decontamination as the $Sr(NO_3)_2$ was available (August 1955).

4. Testing and routine use of 0.0025 M $Fe(CN)_6^{-4}$ and Ni^{+2} instead of 0.005 M (August 1955 test, November 1955 routine).

5. Added Na_2HPO_4 to wastes that were low in PO_4^{-2} concentration to improve Sr-90 retention in soil (January 1956).

The scavenged UR waste was routed to a receiver tank in the BY Tank Farm in 200E Area (usually BY-106, 107, 108, or 110) at a rate up to approximately 50,000 gallons per day. When the tank was full, the waste stream was switched to another receiver tank. The filled tank was allowed to settle for a minimum of one week and was then sampled at several incremental depths and analyzed for pH, Cs, Sr, total β, total α and PO_4. If the Cs and Sr were within limits, the tank was then pumped to a crib/trench via a floating suction pump. Grab samples were taken from the discharge line to the crib/trench for every 50,000 gallons cribbed (100,000 gallons after 6/55), composited and analyzed for the above components plus several others. The pump discharge line had a continuous gamma monitor mounted on it. The pump was to be shut off when a sudden increase in the monitor signal indicated the tank sludge level had been reached. The accumulated sludge in the receiver tanks was periodically transferred to tanks BY-104 or 105. The expected sludge volume was 7-10% of the treated supernate volume.

The UR wastes were scavenged throughout the remainder of the Metal Waste Recovery program. The last scavenged waste from U Plant was received in the 200 East Area in June 1957.

Unscavenged UR waste already stored in 200E Area tanks before scavenging began in U Plant were routed (beginning in May 1955) to the 244-CR vault for scavenging. There the pH was adjusted with HNO_3 and/or NaOH to pH 9 ±1 and $Fe(CN)_6^{-4}$ and Ni^{+2} ion added (generally to 0.005 M each). If laboratory analysis of the feed tank indicated additional Sr-90 decontamination was necessary, calcium nitrate was also added. The scavenged waste was then routed to another tank for settling, sampling and decantation to a crib. Note that this procedure probably left much of the original, alkaline-insoluble solids (e.g., $Fe(OH)_3$) produced from neutralizing the UR waste in the original UR waste storage tanks. The primary receiver tanks for this "in-farm scavenged" waste were C-108, 109, 111, 112. The expected sludge volume from the in-farm scavenging was 10% of the treated supernate volume. In-farm scavenging was completed in December 1957.

The original plans called for cribbing the scavenged supernate. However in 1956 it was found that Co-60 in the supernate would go to the groundwater and exceed allowable limits. Considerable effort was expended trying to develop a cobalt scavenging procedure while disposal to ground was held up. Eventually it was decided to dispose the high Co-60 wastes to ground on a specific retention basis (10/56). A Co-60 scavenging flowsheet was used on some in-farm scavenging campaigns. This procedure involved adding Na_2S to 0.003M in the waste after adjusting the pH to 8.5-9.2, and then proceeding with $NiSO_4$ and $Na_4Fe(CN)_6$ additions.

There were plans to do in-farm scavenging of the 200W Area UR waste also. A project for chemical addition facilities at the 242-T evaporator and laboratory studies were completed. However no in-farm scavenging in 200 West area was performed. The reason may have been that conditions for cribbing and/or specific retention disposal in the 200 West areas were not very favorable. The height of the soil column (surface to groundwater) at the BC crib site was approximately 340 feet which was much greater than under the 200 West or East areas. Examination of records for waste disposed to ground for both 200E and 200W Areas do not show ground disposal in 200W Area of scavenged wastes other than those noted below.

The records for scavenged waste in 200W Area include the U Plant test in late 1953 where the treated supernate was routed to T-101, and in-plant scavenging of first cycle T Plant supernates which were subsequently routed to TY tanks 101, 103, and 104. (A total of 6 batches, with a total of 2.93 million gallons disposed to TY cribs.)

The T Plant test used 0.005 M $K_4Fe(CN)_6$ added to the acid waste, pH adjustment to 9 ±1, addition of $NiSO_4$ to 0.005 M. Coating waste was to be combined with the scavenged waste either in the T Plant or underground waste tank. It was planned to scavenge 750,000 gallons of first cycle wastes in the initial plant test. Later information indicates that incorporation of the coating waste into the IC scavenged waste gave poor decontamination so the two waste types were segregated. Routine scavenging of T Plant IC wastes started on December 31, 1954 and continued until T Plant was shut down in August 1956.

The effective reduction in waste volume, as discharged from the building was approximately 88%. Note that the first cycle waste would contain less than 10% of the fission product Cs-137 and Sr-90 that would be in the original charge. The metal waste contained 90+% of the fission products.

ATTACHMENT N

GENERAL ELECTRIC COMPANY

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HW-30399

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By T. Burks DATE 10-16-90
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23. C. A. Rohrmann
24. G. Sege
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January 8, 1954

TO: C. A. Rohrmann
FROM: R. J. Sloat

TBP PLANT NICKEL FERROCYANIDE SCAVENGING FLOWSHEET

INTRODUCTION

Recent plant-scale scavenging and cribbing tests have confirmed laboratory data which indicated that the cesium and strontium in TBP wastes could be reduced by nickel ferrocyanide scavenging to concentrations which permit discharge of the scavenged supernatant to cribs. In this document a chemical flowsheet is presented for use as a design basis for facilities which will permit scavenging of unconcentrated neutralized waste for the TBP Plant.

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DISCUSSION

Waste Volume. The combined waste volume shown on the attached flowsheet has been calculated from the HW No. 6 TBP Flowsheet. It represents the waste volume which might be expected if flowsheet beds were consistently

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processed in the plant. Since the TBP Plant feed composition varies considerably from batch to batch the volume of waste produced from the plant has been greater than the flowsheet value. Past plant experience indicates that cribs and sludge storage facilities should be sized to handle volumes as much as 20% greater than the volumes shown on Figure 1. If the facilities for waste scavenging are available by April, 1954, approximately 3000 tons of uranium will remain to be processed in the TBP Plant. Consequently, 25 to 35 million gallons of neutralized-scavenged waste will be discharged from the TBP Plant to the settling tanks. The bulk of this waste will be discharged to cribs. Approximately 2.5 to 3 million gallons of sludge would be permanently stored.

Storage of Scavenged Waste. As is indicated on Figure 1, the sludge from the scavenged waste contains at least half of the uranium* and essentially all of the Sr and Cs originally present in the TBP wastes. Since it may be desirable in the future to recover the uranium and/or the Cs and Sr from the sludge (preliminary laboratory feasibility studies are currently in progress), the tankage presently equipped with sludge removal facilities should be used for the scavenged wastes. In addition, the number of cascades used for storage should be kept low, so that any future removal operations would be confined to a few cascades.

Fission Product Concentrations. Although the major portion of the uranium remaining to be processed through the TBP Plant is aged greater than one year, this figure has been chosen as the calculation basis for the flowsheet. In calculating the fission product concentrations it was assumed that the uranium was subjected to an integrated pile exposure of 600 MWD/ton and that the pile power level was 2.2 Megawatts/ton.

Laboratory data have not been obtained which permit prediction of the relative amounts of short-lived fission products in the supernate and sludge. Although the concentrations of the short-half-life fission products in the supernate are unimportant from a cribbing standpoint (these fission products decay to a tolerable level before reaching the water table.), they are important in designing the shielding (surface or buried lines) for the lines leading to the cribs. For the 1-year-aged waste of the flowsheet, the gross gamma concentration of the supernate could be as high as 2 curies/gal. with Ru^{106}, Zr^{95}, and Nb^{95} all contributing approximately the same amount to the total.

Sludge Heating. Calculations have been made to determine the amount of heat which will be evolved in the tanks containing the sludge from the scavenging operation. From the calculations it is concluded that a tank full of sludge may be stored without boiling as long as the minimum age of the waste (time since pile discharge) is two years. When the age of the scavenged waste decreases below two years, the sludge should not be

---

*) At pH 8.5 to 9 the supernate from waste scavenging contains approximately 0.15 g.U/l. With a 1% Plant loss, it is estimated that half the uranium will be precipitated with the sludge. At higher TBP Plant uranium waste losses a greater portion of the uranium originally present in the combined waste will be precipitated in the sludge.

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allowed to accumulate in the first tank of a cascade. Instead, the sludge and supernate should be discharged together into storage tanks where settling may occur. When the waste has "cooled" sufficiently, the supernatant may be decanted and the tanks refilled with other wastes. The amount of waste to be stored in this manner will be relatively small. If an average Bismuth Phosphate processing rate of 15 tons/month is assumed from July 1, 1953, until July 1, 1955, the waste resulting from processing approximately 360 tons of uranium through the TBP Plant must be temporarily stored. If this waste were stored as neutralized, unconcentrated scavenged waste, approximately 3 million gallons of storage space would be temporarily required. Only approximately 300,000 gallons of this space would be eventually required for permanent storage of the iron hydroxide and nickel ferrocyanide sludge after decanting and cribbing the supernate.

In arriving at the above conclusions regarding sludge heating, certain safe-side assumptions were made, as follows:

1. It was assumed that all the fission products present in the TBP waste would be precipitated with the ferrocyanide slurry. Actually, a good portion (probably greater than 50%) of the short-lived fission products will be discharged to cribs in the supernatant.

2. It was assumed that the slurry would settle to a final sludge storage volume of approximately 300 gal./ton of uranium processed through the TBP Plant. This settled volume is approximately 40% of the sludge volume shown on Figure 1. Although the flowsheet volume is believed to be realistic, the smaller volume was used in sludge heating calculations to allow for compacting in the tank and to permit later flowsheet changes which may reduce the sludge volume (e.g., substitution of oxalate for iron in the RA Column.)

3. It was assumed that a 550,000 gallon waste storage tank would be filled with sludge greater than two years old. It was assumed the sludge will be produced from the available wastes aged as close to 2 years as possible. In actual plant practice, presumably wastes will be alternated from one cascade to another. Consequently, wastes aged approximately two years would be mixed with older sludges.

4. It was assumed that heat losses to the ground from the 550,000 gal. tank would be approximately 400,000 Btu/hr. at the period of peak heat evolution.

Scavenging or Previously Stored TBP Waste. The above discussion applies to the scavenging of wastes to be produced by the TBP Plant after the required plant modifications are completed in March or April, 1954. As storage volume is made available by scavenging current TBP wastes, the way will be opened for scavenging of the approximately 18 million gallons of unscavenged neutralized concentrated waste already produced from TBP processing of 3,300 tons of uranium. (Of this 18 million gallons, approximately 8 million gallons will have been concentrated to approximately 5 million gallons in the 1st cycle waste evaporation). A tentative method to be used

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for scavenging of these wastes involving the use of the TBP tank farm mining and waste acidification facilities was presented in HW-28715, Copper Ferrocyanide Scavenging of TBP Wastes. Since uranium removal operations will soon be completed in "C" and "U" Farms, dissolution facilities in these farms could be used for treatment of the unscavenged wastes.

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Figure 1

NICKEL FERROCYANIDE SCAVENGING OF TBP PLANT WASTE

Potassium Ferrocyanide Add'n.(5)

$K_4Fe(CN)_6 \cdot 3H_2O$	0.5 M
Flow (RAF = 100)	1.9
Flow (gal./ton U)	71

NaOH Addition

NaOH	19 M
Flow (RAF = 100)	20
Flow (gal./ton U)	750

Nickel Sulfate Addition(5)

$NiSO_4 \cdot 6H_2O$	1.2 M
Flow (RAF = 100)	0.8
Flow (gal./ton U)	30

Combined Waste Receiving and Sampling

RAF Flow 145

Combined RC Column wastes Flow 26

	M
$SO_4^=$	0.20
$PO_4^{\equiv}$	0.15
NO_3^-	3.72
K^+	2.13
Na^+	2.43
$K_4Fe(CN)_6$	0.0056
$Fe(NH_4)_2(SO_4)_2$	0.017
H_2NSO_3	0.034
UEH	0.0015

	Beta	Gamma
Cs^{137} curies/gal.	0.27	0.27
Sr^{90} curies/gal.	0.75	—
Gross curies/gal.(1)	13	2.5

Flow (RAF = 100)	173
Flow (gal./ton U)	6450

Waste Neutralization

	M
$SO_4^=$	0.24
$PO_4^{\equiv}$	0.13
NO_3^-	3.33
Na^+	4.15
NH_4^+	0.06
$K_4Fe(CN)_6$	0.005
$Fe(OH)_3$	0.015
$Na_2U_2O_7$	0.007

pH = 8.5 +1.5 −0.5

Flow (RAF = 100)	193
Flow (gal./ton U)	7200

Scavenger Formation Neutralized Waste

	M
$SO_4^=$	0.24
$PO_4^{\equiv}$	0.13
NO_3^-	3.30
Na^+	4.10
K^+	0.01
NH_4^+	0.06
$Ni_2Fe(CN)_6$	0.0025
$K_4Fe(CN)_6$	0.0025
$Fe(OH)_3$	0.015
$Na_2U_2O_7$	0.0007

Flow (RAF = 100)	194
Flow (gal./ton U)	7230

Settling

Supernate to Cribs

	M
$SO_4^=$	0.27
$PO_4^{\equiv}$	0.14
NO_3^-	3.68
Na^+	4.55
K^+	0.02
NH_4^+	0.07
U	0.0078(6)
Cs D.F.	≥ 500
Sr D.F.	≥ 200

	Beta	Gamma
Cs^{137} curies/gal.	≤ 5 x 10^{-4}	≤ 5 x 10^{-4}
Sr^{90} curies/gal.	≤ 4 x 10^{-4}	—
Gross curies/gal. (See Note 2)		

Flow (RAF = 100)	175
Flow (gal./ton U)	6510

Stored Sludge

	M
$Fe(CN)_6^{\equiv}$	0.0025
$Ni_2Fe(CN)_6$	0.0025
$Fe(OH)_3$	0.15
$Na_2U_2O_7$	0.0035(6)

	Beta	Gamma
Cs^{137} curies/gal.	2.4	2.4
Sr^{90} curies/gal.	6.6	—
Gross curies/gal.(2)	110	22

Sludge Volume (RAF = 100)(3)	≤ 19.5
Sludge Volume (gal./ton U)(3)	≤ 725

NOTES:

(1) Although the age of most of the TBP Plant wastes will be at least two years, it is possible that waste aged less than one year may be processed. Fission product concentrations are based on a 1 year aged waste produced from 6.7 MWD/ton uranium (2.2 megawatts/ton – 850 day pile exposure assumed).

(2) The proportion of the short half-life fission products remaining in the sludge has not been determined. Presumably a relatively large portion of the ruthenium, zirconium, and niobium will be discharged to cribs. In the flowsheet above, it has been assumed that all the short-lived fission products end up in the sludge, resulting in a conservative calculation of heating effects in the waste storage tanks.

(3) The sludge volume shown above is conservative (i.e., greater than the volume which will be stored) and is quoted to permit calculation of the maximum sludge storage capacity. With flowsheet modifications (e.g., substitution of oxalate for ferrous ammonium sulfate and sulfamic acid in the RA Column, and/or reduction of scavenger concentrations) and packing of sludge in the storage tanks, the volume of sludge stored may be decreased to approx. 300 gal./ton of U processed. This smaller volume has been used in estimating maximum heating effects in the sludge layer.

(4) Essentially all of the ferrocyanide will be present in the sludge. The anions associated with the ferrocyanide are not positively known. Cesium and iron complexes are believed to be formed.

(5) Potassium ferrocyanide and nickel sulfate additions should be varied with the volume of waste produced. Sufficient potassium ferrocyanide and nickel sulfate should be added to produce 0.005 M ferrocyanide and nickel concentrations in the composite scavenged waste sent to settling tanks.

(6) If the TBP Plant uranium waste loss is 1% of the U processed, approximately half of this uranium is found in the stored sludges as indicated above. At higher plant uranium waste losses the supernate uranium concentration is not expected to increase. Consequently, a greater portion of the uranium present in the Plant Waste is found in the stored sludges as Plant uranium losses increase above 1%.

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ATTACHMENT O

FIGURES, FERROCYANIDE STUDY

L. L. Burger
February 8, 1991

Fig. 1 Typical conditions and probable precipitates.
Fig. 2 Representative Reactions, Products and maximum energies.
Fig. 3 Enthalpy of formation, cyanides.
Fig. 4 Explosive Data
Fig. 5 LANL Tests for PNL.
Fig. 6 Typical thermogravimetric analysis of reaction.
Fig. 7 DSC, Air oxidation, (composition of sodium salt has not been confirmed).
Fig. 8 DSC, Comparison of oxidation with nitrate salt and with mixed nitrate-nitrite (Composition of nickel salt has not been confirmed)
Fig. 9 DSC of nickel salt after contact with dilute NaOH. (Prepared from colloidal precipitate).
Fig. 10 Effect of scan rate on DSC. Used for calculation of kinetic parameters.
Fig. 11 Typical time-to-explosion test.
Fig. 12 TTX plots of various mixtures. Dashed line is cesium nickel ferrocyanide with 50/50 sodium nitrate/sodium nitrite. Line labeled Cs_2, 5% EDTA is cesium nickel ferrocyanide with 5% EDTA added to nitrate-nitrite mix. Remaining data are for nickel ferrocyanide (not yet analyzed). P&B is Pfaltz and Bauer commercial $Ni_2Fe(CN)_6$.
Fig. 13 Comparison of ferro- and ferri-cyanides. Compounds have not yet been confirmed. All nickel ferrocyanides are probably non-stoichiometric.
Fig. 14 Results of TTX tests. "t at 360°" is the time to explosion at 360°C. "Tc" is the estimated critical explosion temperature for the sample geometry used.
Fig. 15 Kinetic data from Figure 10. Methods of determination of E_a include 1) isothermal rate measurements at different temperatures, 2) From DSC by incremental ΔH measurements, from DSC runs at different scan rates by ASTM method or by Kissinger method. The latter was used here.
Fig. 16 Typical activation energies for explosive reactions.
Fig. 17 Representation of thermal runaway conditions.
Fig. 18 Experimental temperature in 5 mm tube containing explosive mix. The time to explosion with the thermocouple in place is much longer than seen from Fig. 14 due to heat loss through the thermocouple.
Fig. 19 Log plot of TTX data using arbitrary temperature lag correction.
Fig. 20 Calculated dilution effects using heat capacity and transition data.
Fig. 21 Calculated energy required to heat 1 g of various substances.
Fig. 22 Dissociation and solubility data.
Fig. 23 Radiolysis showing one potential route to ferrocyanide destruction.
Fig. 24 Radiation yields and the effect of high pH on radiolytic products.
Fig. 25 Present PNL program.

Formation of Cyanide Solids in Waste Tanks

Conditions

3-6M $NaNO_3$

1-3M $NaNO_2$

pH 9.3 ± 0.5

0.005M $Na_4Fe(CN)_6$, K_4 –

0.005M $NiSO_4$

Precipitates

$Ni_2Fe(CN)_6$

$Na_2NiFe(CN)_6$

$Cs_2NiFe\ (CN)_6$

$(Na,K,Ni)\ Fe(CN)_6$

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Energetics of Potential CN Reactions

Typical:

$$Na_2NiFe(CN)_6 + 6NaNO_3 \rightarrow FeO, NiO, N_2, CO_2, Na_2CO_3$$

$$\Delta H = -3015 \text{ kJ}, 502 \text{ kJ/CN}$$

Reactant[1]	Oxidant	Products	Mols gas/C	kJ/C
Na_2NiF	$NaNO_3$	N_2, CO_2, Na_2CO_3	1.33	–502
Na_2NiF	$NaNO_3$	N_2, CO_2, Na_2O	2.0	–287
Na_2NiF	$NaNO_2$	N_2, Na_2CO_3	1.33	–618
Ni_2F	$NaNO_3$	N_2, CO_2, Na_2CO_3	1.5	–480
Ni_2F	$NaNO_2$	N_2, CO_2, Na_2CO_3	1.33	–580
NaCN	$NaNO_3$	N_2, Na_2CO_3	1.0	–575
Na_2NiF	$NaNO_3$	N_2, CO, Na_2O	1.8	–40
Na_2NiF	$NaNO_3$	NO, CO_2, Na_2O	4.3	+361
$NaCH_3COO$	$NaNO_3$	N_2, CO_2, Na_2CO_3, H_2O	1.1	–325

[1] F = Fe $(CN)_6$

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0.3

ΔH_f of $Fe(CN)_6$ Compounds

Cpd	ΔH_f/CN, kJ	
$Fe_4[Fe(CN)_6]_3$	+55.7	
$Zn_2\ Fe(CN)_6$	$+71 \pm 10$	est. from dihydrate
$Ni_2\ Fe(CN)_6$	$+58 \pm 10$	est. from dihydrate
$K_4\ Fe(CN)_6$	–99	
$K_3\ Fe(CN)_6$	–42	
$Cu_2\ Fe(CN)_6$	$+123 \pm 20$	
NaCN	–88	
CuCN	+96	
AgCN	+146	
$Ni(CN)_2$	+64	

$\Delta H_f\ Ni_2Fe(CN)_6 = +250\ (40 \pm 20/CN)$

$\Delta H_f\ Na_2NiFe(CN)_6 = 0\ (0 \pm 20/CN)$

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0.4

Explosive Data

Material	kCal/g	Theoret. kJ/g	Expt'l kJ/g	Mols gas/kg
RDX	1.48	6.19	–	40
PETN	1.51	6.32	5.73	38
TNT	1.29	5.40	4.27	
DATB	1.15	4.81	3.81	
$Na_2NiFeCN$ $Na(NO_3, NO_2)$	0.88	3.70	2.78[a]	9-15

[a]Estimated

Ferrocyanide Reaction Studies

Planned LANL Activities

For one mixture of FeCN and Oxidant:

- Safe handling evaluations
  - Non-thermal tests
    - Shock sensitivity
    - Spark sensitivity
    - Friction sensitivity
  - Thermal tests
    - Thermal behavior
    - Thermal decomposition behavior
    - Vacuum stability at 120 °C
    - Small-scale thermally-induced explosion behavior
    - Effect of increasing mass and bulk (ARC test)
- Large-scale test
  - Effect of increased mass and bulk (2 kilogram)

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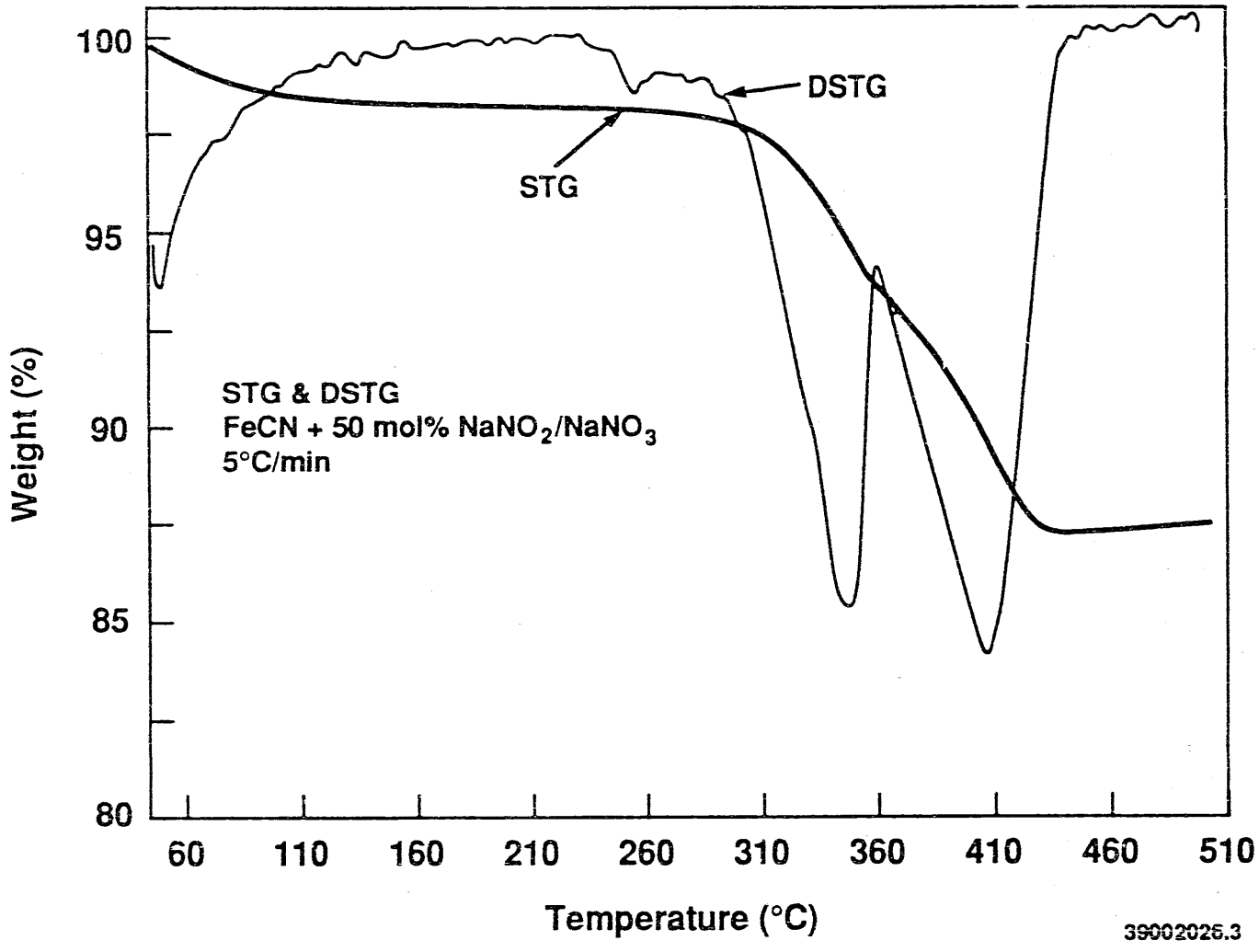
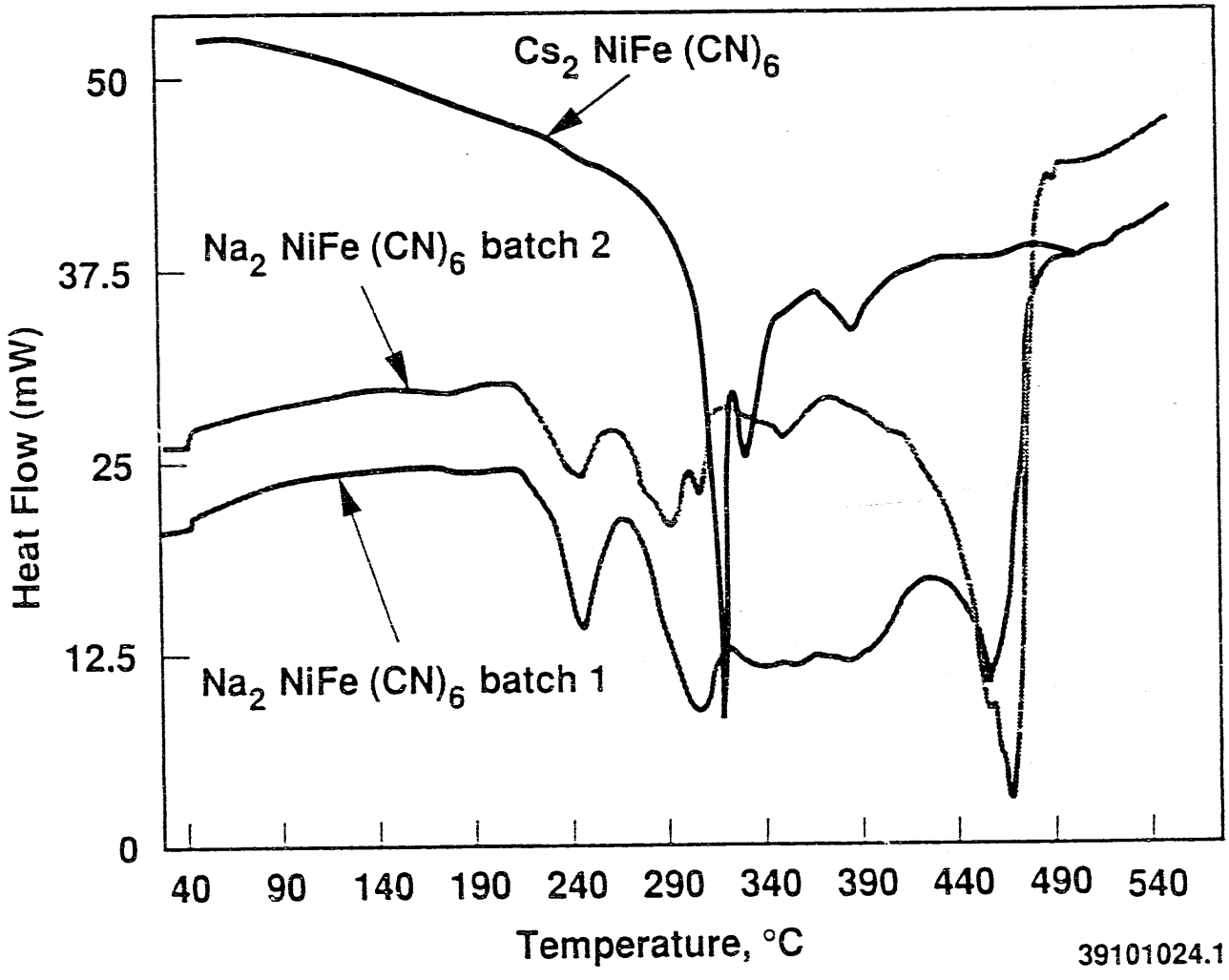
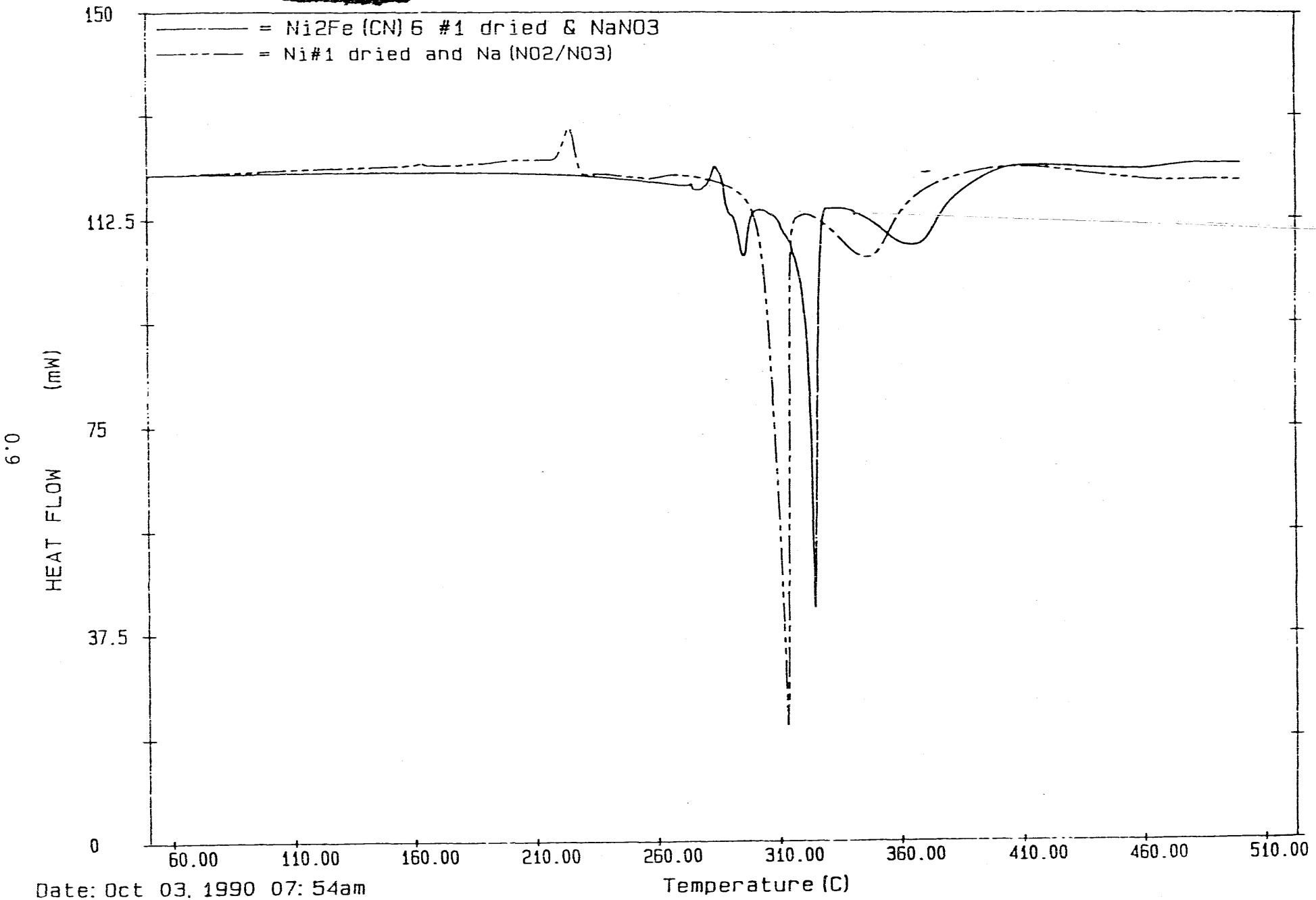

100
95
90
85
80
Weight (%)
60
110
160
210
260
310
360
410
460
510
Temperature (°C)
DSTG
STG
STG & DSTG
FeCN + 50 mol% NaNO2/NaNO3
5°C/min
39002026.3

DSC Analysis of The Air Oxidation of Sodium Nickel Ferrocyanide and Cesium Nickel Ferrocyanide





Date: Oct 03, 1990 07:54am
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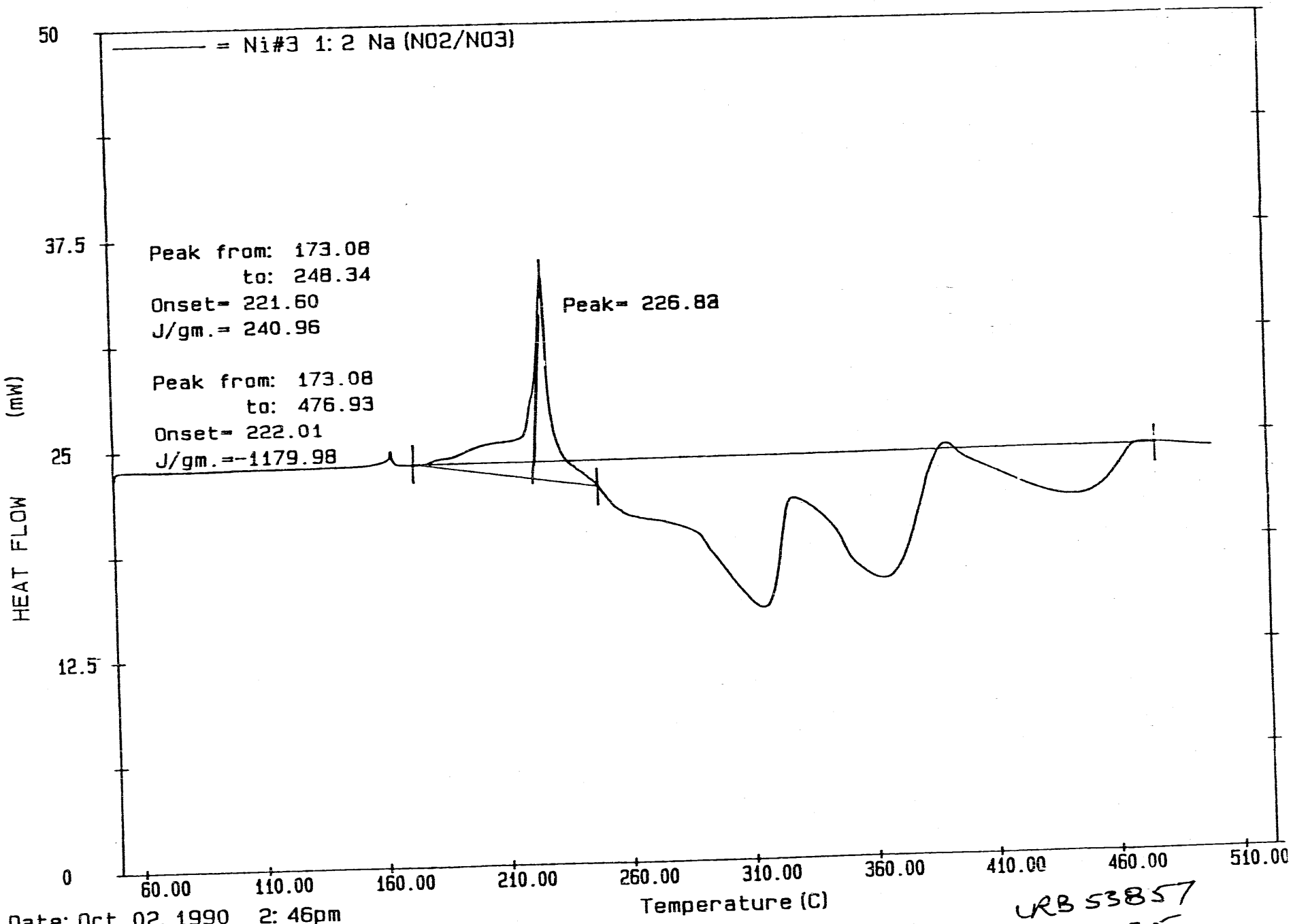
Sample Wt: 6.500 mg Path: A:\
File: DSC091 R L SELL

PE PC SERIES DSC7

6.0



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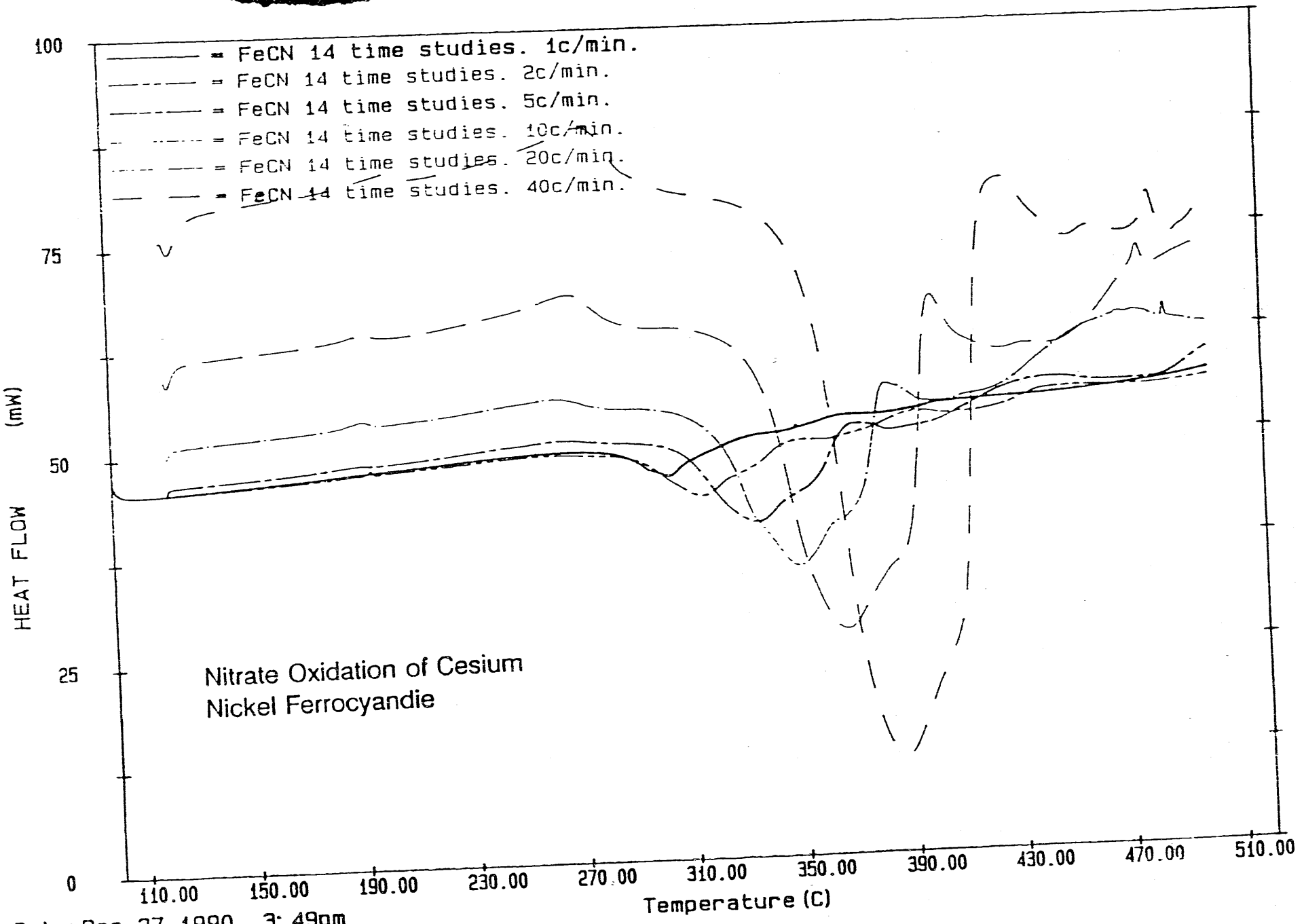
Samole Wt: 7[redacted]

URB 53857
p.135



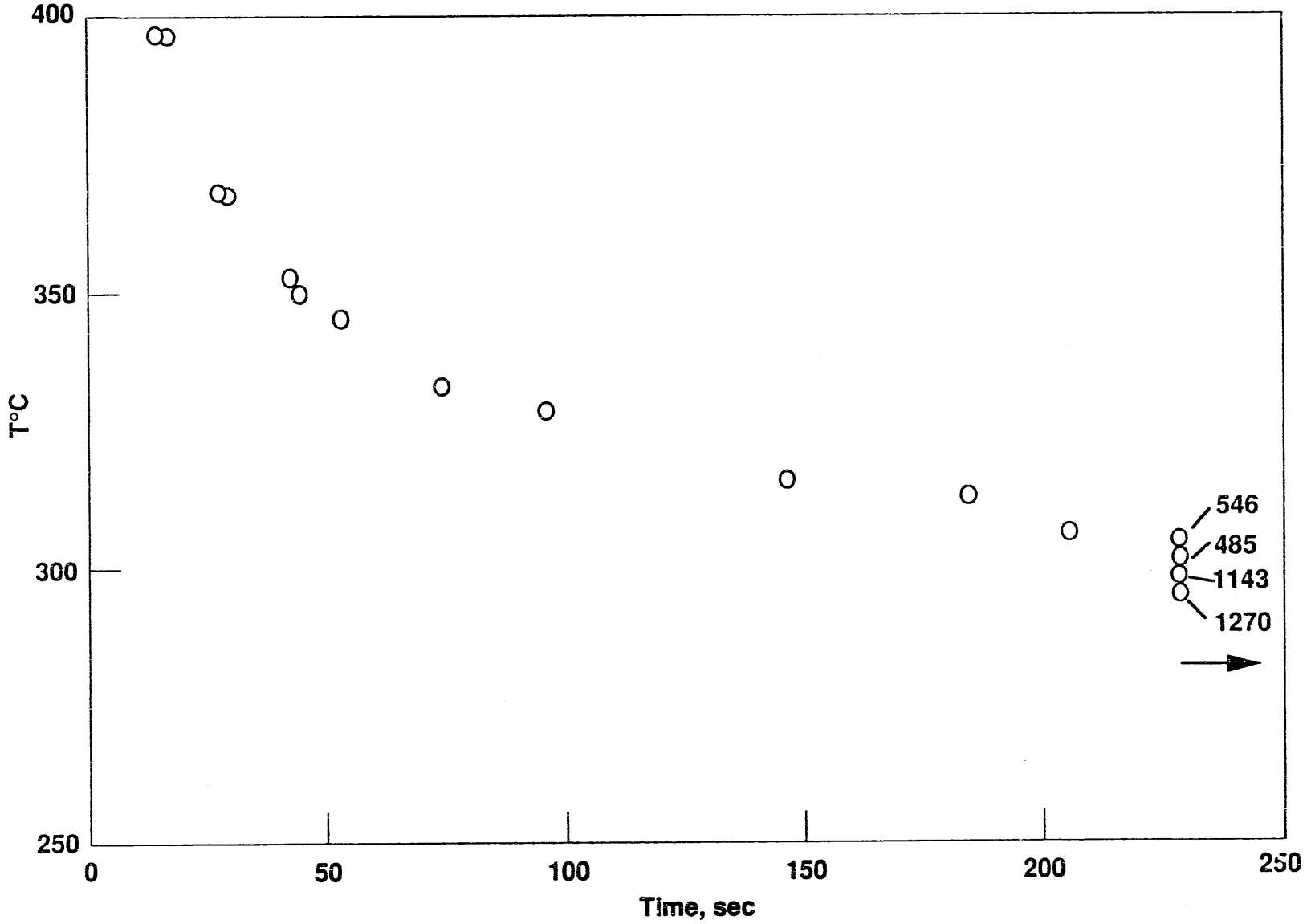
Date: Dec 27, 1990 3: 49pm
Scanning Rate: 1.0 C/min
Sample Wt: 6.000 mg Path: \pe\
File: TS01 R 1 SF11

PE PC SERIES DSC7

0.11

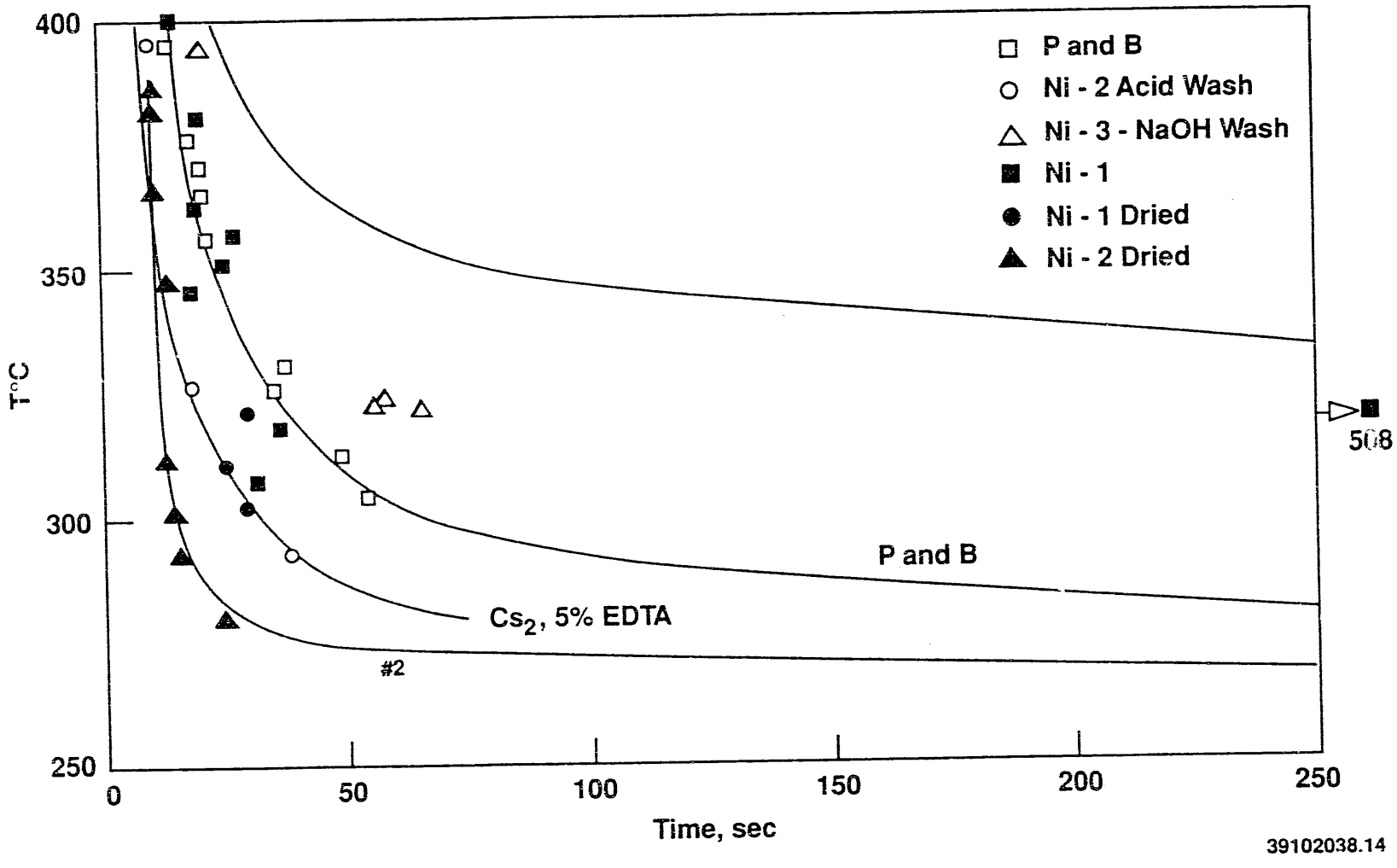
TTX

FeCN - 65 $NaNO_2$ -35 KNO_2

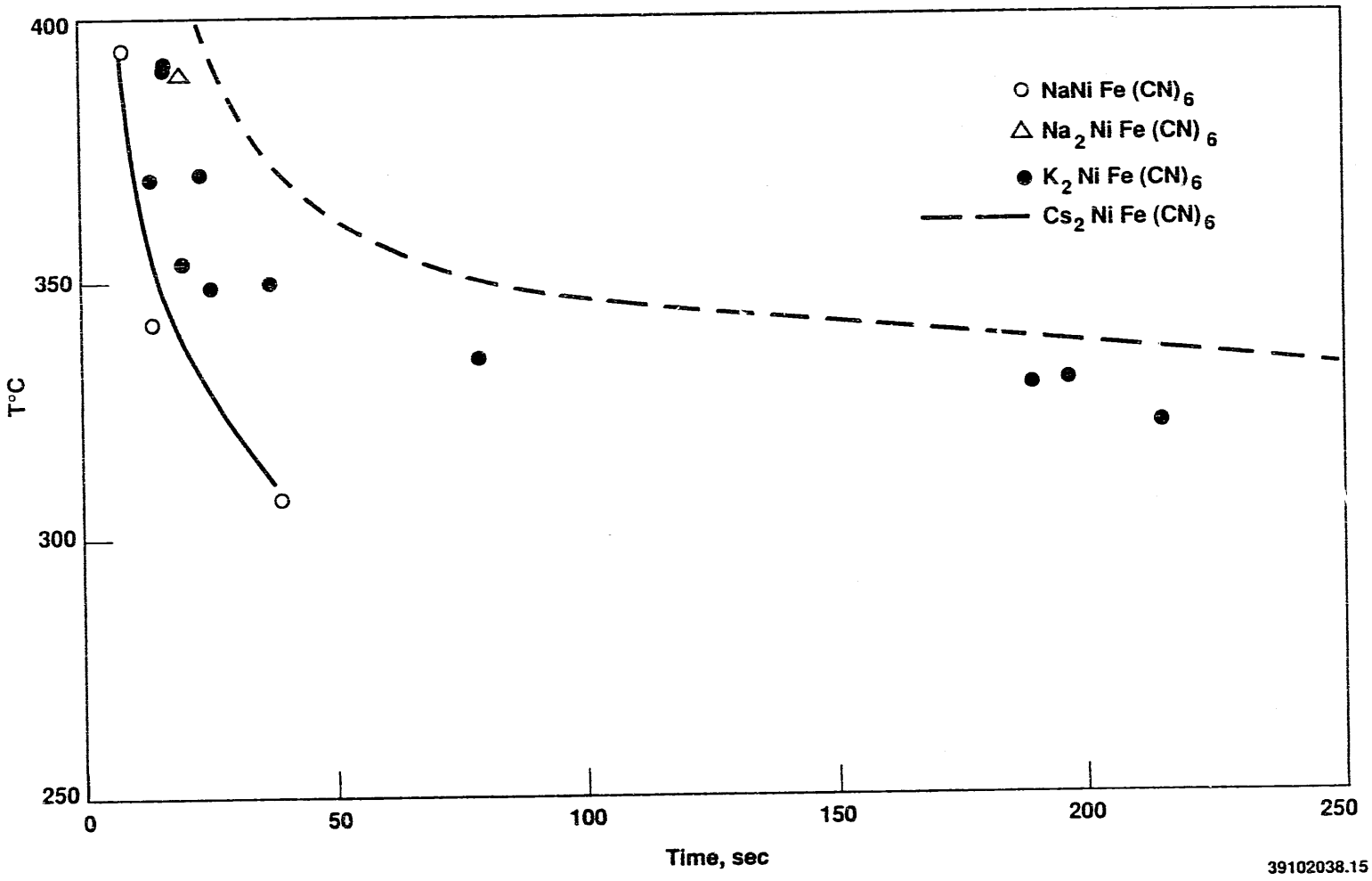


39102038.17

TTX


400
350
300
250
T°C
0
50
100
150
200
250
Time, sec
P and B
Ni - 2 Acid Wash
Ni - 3 - NaOH Wash
Ni - 1
Ni - 1 Dried
Ni - 2 Dried
P and B
Cs_2, 5% EDTA
#2
508
39102038.14

TTX


400
350
300
250
T°C
0
50
100
150
200
250
Time, sec
NaNi Fe (CN)6
Na2 Ni Fe (CN) 6
K2 Ni Fe (CN)6
Cs2 Ni Fe (CN)6
39102038.15

Small Scale Explosion Behavior of Some Cyanides

Compound	Oxidant	M.P.	t, sec, 360°	Tc, est, °C
Cs_2Nif	$(Na,K)NO_3$	154	15	310 ± 10
Cs_2Nif	$(Na,K)NO_2$	223	33	300 ± 5
Cs_2Nif	$Na(NO_3,NO_2)$	227	50	340 ± 10
Cs_2Nif	$Na(NO_3,NO_2)$ 5% $Ni(OH)_2$	227	18	300 ± 5
Cs_2Nif	$Na(NO_3,NO_2)$ 5% EDTA	227	8	280 ± 5
KCN	$(Na,K)NO_2$	223	240	350 ± 20
Na_2Nif	$Na(NO_3,NO_2)$	227	27	330 ± 10
Ni_2f	$Na(NO_3, NO_2)$	227	10	280 ± 10
NaNif-3	$Na(NO_3,NO_2)$	227	13	300 ± 10
$NaCH_3COO$	$Na(NO_3,NO_2)$	227	–	435 ± 10

f = ferrocyanide; f-3 = ferricyanide

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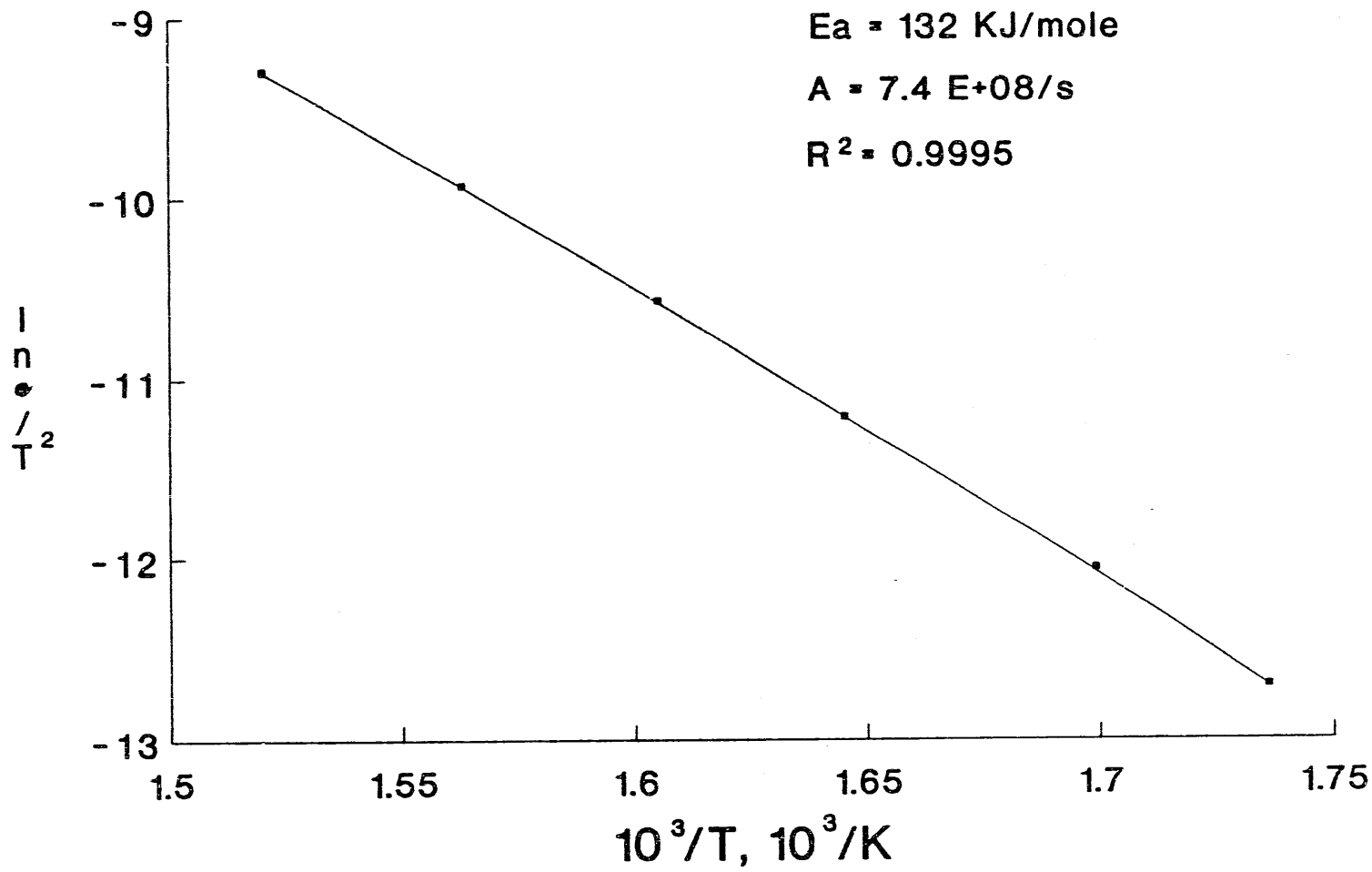
Arrhenius Plot of DSC Data
Cesium Nickel Ferrocyanide + Nitrate



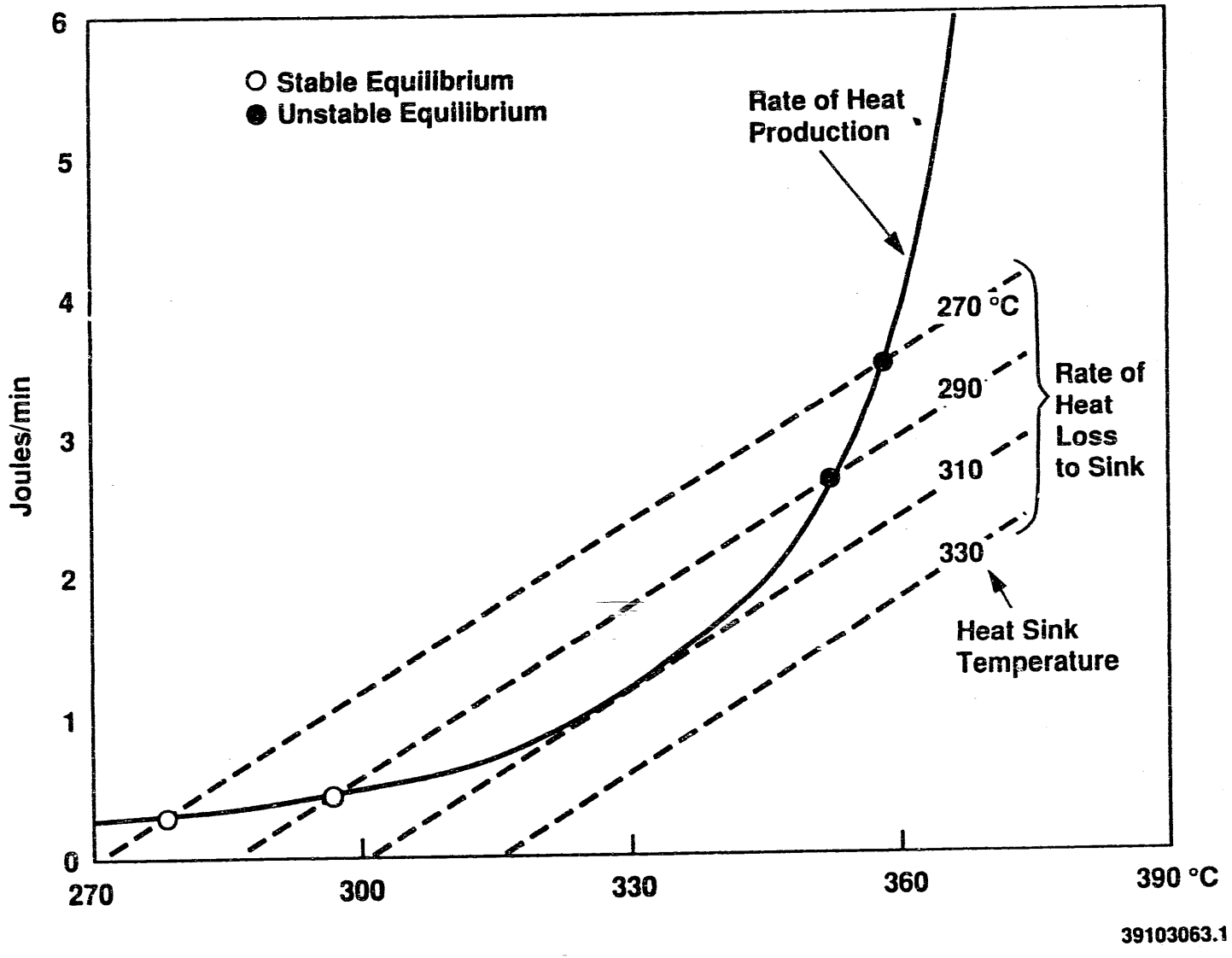
January 10, 1991

Ferrocyanide Reaction Studies

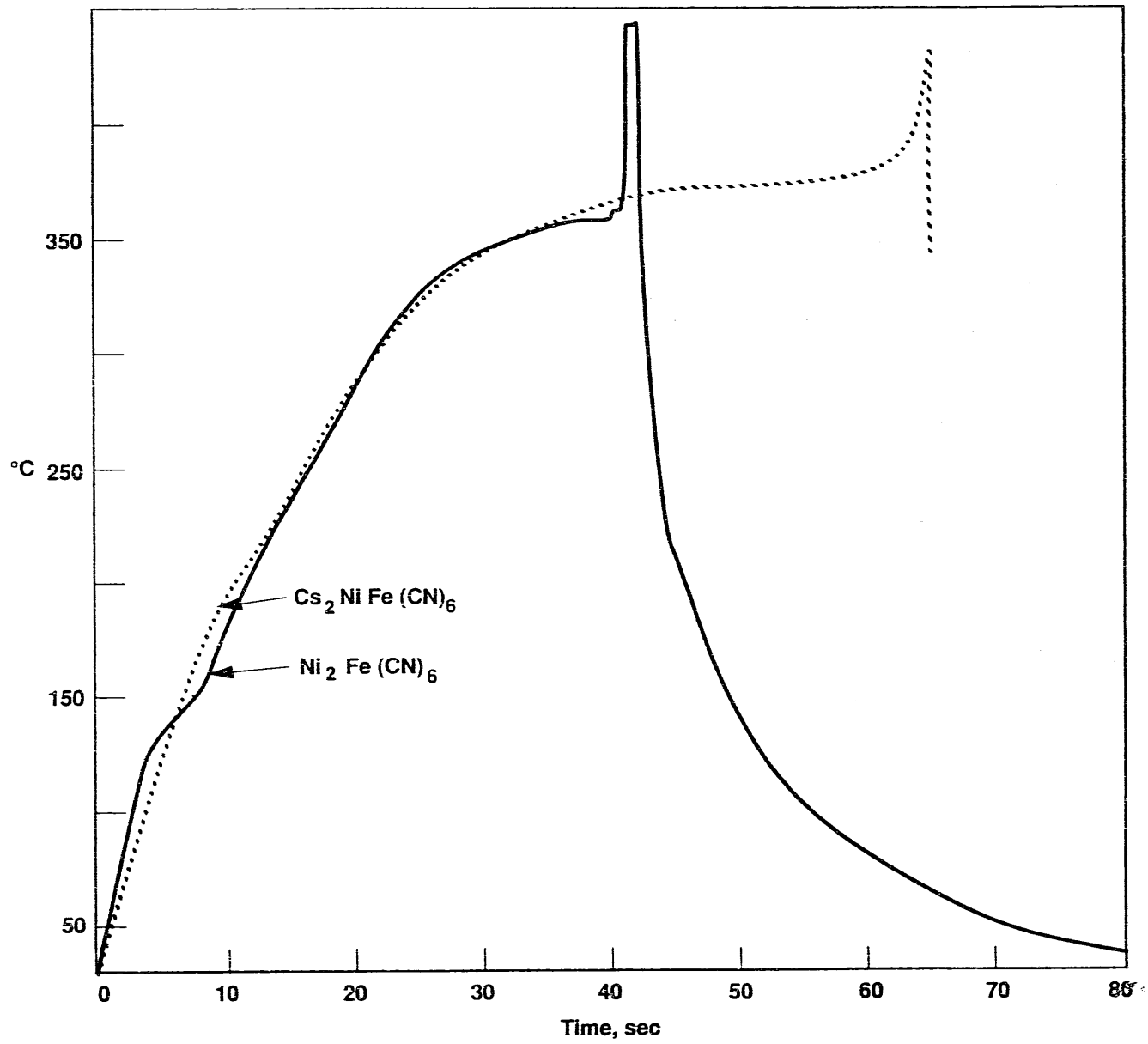
Activation Energies

Material	Ea, KJ/mole	Method, Source
$Cs_2NiFe(CN)_6/NaNO_3$	132	DSC, PNL
$Cs_2NiFe(CN)_6/Na,KNO_2$	98	DSC, PNL
TATB	251	DSC, Rogers
TNT	143	DSC, Rogers
$Hg(ONC)_2$	117	DSC, Whelan

January 10, 1991


Stable Equilibrium
Unstable Equilibrium
Rate of Heat Production
270 °C
290
310
330
Rate of Heat Loss to Sink
Heat Sink Temperature
Joules/min
0
1
2
3
4
5
6
270
300
330
360
390 °C
39103063.1

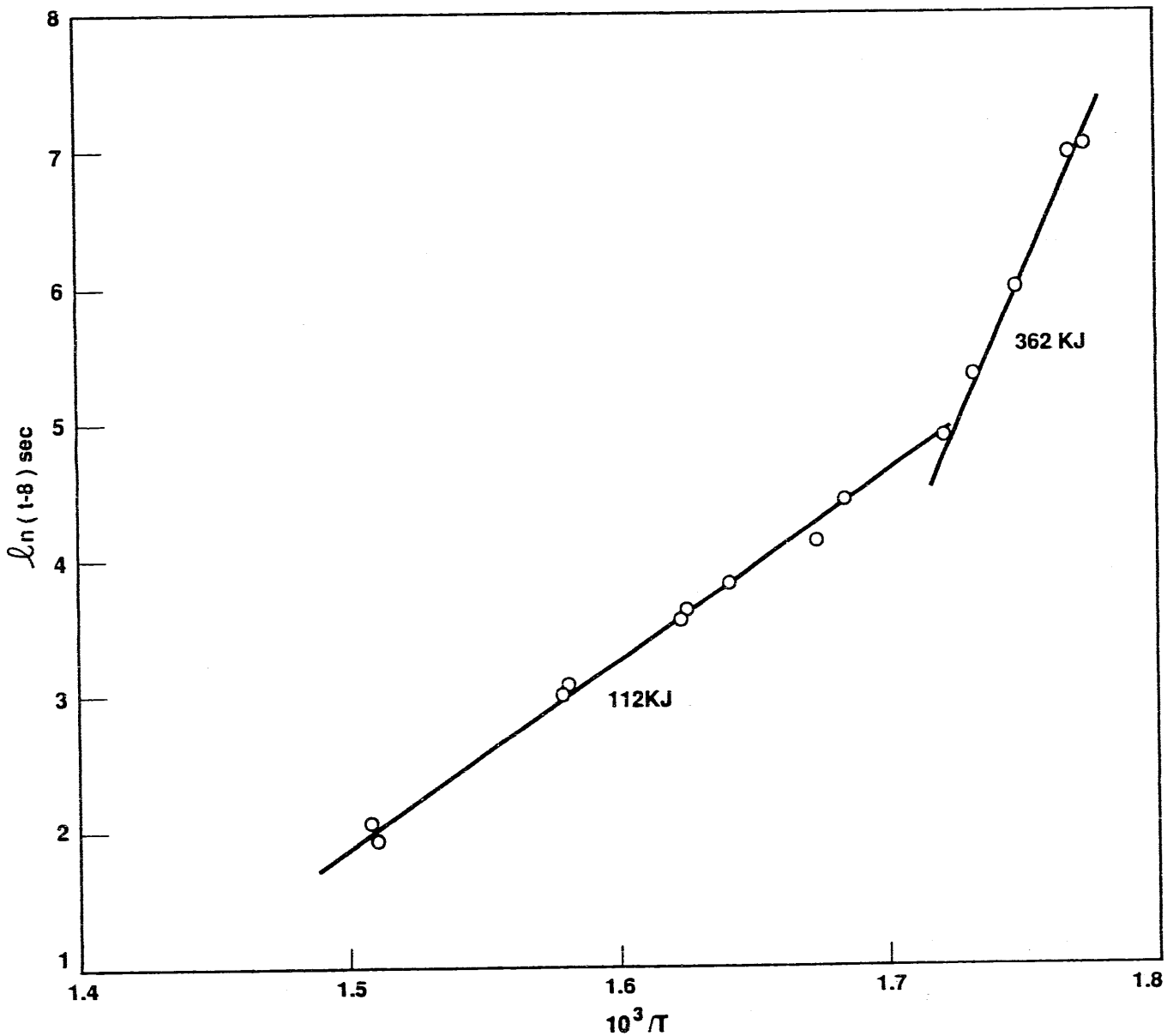
Temperature - Explosion Curve Block 360° C



39102038.16

TTX

$Cs_2 Ni Fe (CN)_6$-Na, K (NO_2)



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Dilution Effects

Effective ΔH, 7.92 kJ/g $Na_2NiFe(CN)_6$
2.78 kJ/g stoich mix of nitrate-nitrite
Based on 75% efficiency

<u>Endothermic steps</u>

$60° \rightarrow 100°$, $\Sigma \int CpdT$
Evaporate H_2O, 540 cal/g
$100° \rightarrow 300°$, $\Sigma \int CpdT$
Melt $NaNO_3$, 44.7 cal/g
$300° \rightarrow 800°$, $\Sigma \int CpdT$
Decompose nitrate,
$800° \rightarrow 1800°$, $\Sigma \int CpdT$
Decompose Na_2CO_3
$1800° \rightarrow T_f$, $\Sigma \int CpdT$ oxides, gases

Possible Heat Sinks in Tanks

Substance	Temperature Reached 100° (373 K)	307° (580 K)	507° (780 K)
H_2O	584	698	818
$NaNO_3$	–	161	290
$NaAlO_2$	–	81	147

3g H_2O, 14g $NaNO_3$(10g if Molten), or 24g $NaAlO_2$ per g of $Na_2NiFe(CN)_6$ would prevent propagation of reaction.

K_{sp},	$Fe(OH)_3$	1.1 E-36
	$Fe(OH)_2$	1.64 E-14
	$Ni(OH)_2$	1.0 E-18
	$Ni_2Fe(CN)_6$	1.2 E-15?
K_{dissoc},	$Fe(CN)_6^{4-}$	2.5 E-36
	$Fe(CN)_6^{3-}$	2.5 E-44
	$Ni(CN)_4^{2-}$	5.0 E-31
k_{hydrol},	$Fe(CN)_6^{4+}$	1.8 E-22
	$Fe(CN)_6^{3-}$	2.5 E-8

$$Fe^{3+} + Fe(CN)_6^{4-} \rightarrow Fe^{2+} + Fe(CN)_6^{3-}$$

$$K = 8.6\ E{+}6$$

$$\frac{Fe(CN)_6^{3-}}{Fe(CN)_6^{4-}} = 5.8\ E{-}13,\ pH = 11$$

$$= 5.8\ E{-}10,\ pH = 8$$

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In Absence of Other Factors, $Fe(CN)_6^{4-}$ is Stable But Radiation May Be a Factor. Example

$H_2O \rightarrow OH + H + e^-_{aq}$

$2OH \rightarrow H_2O_2$

$OH + Fe^{2+} \rightarrow Fe(OH)_3$

$H_2O_2 + Fe^{2+} \rightarrow Fe(OH)_3$

$(H_2O_2 \rightarrow HO_2^- + H^+, K = 2.4\ E\text{-}12)$

$H_2O_2 + CN^- \rightarrow CNO^- + H_2O$

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Gamma Radiation Yields (G)

H_2	H	e^-aq	H_2O_2	HO	HO_2	H^+
0.43	0.61	2.7	0.61	2.86	0.03	2.7

<u>Other RX's</u>

$H + HO \rightarrow H_2O$

$H + H \rightarrow H_2$

$e^-aq + H \rightarrow H_2 + OH^-$

$OH + H_2O_2 \rightarrow HO_2 + H_2O$

$HO_2 + OH \rightarrow H_2O + O_2$

$2HO_2 \rightarrow H_2O_2 + O_2$

$2\ e^-aq \rightarrow H_2 + 2OH^-$

$HO \leftrightarrow H^+ + O^-$ pK = 11.7

$H_2O_2 \leftrightarrow H^+ + HO_2^-$ pK = 11.75

$HO_2 \leftrightarrow H^+ + O_2^-$ pK = 4.4

39102066.1

Present Program

- Preparation and Characterization of Fe CN precipitates
  - Elemental analysis, XRD
  - Stability to OH^-
  - Stability to oxidation
  - Stability to radiolysis(1)
- Thermal studies
  - DSC, TGA, TTX
  - Diluent effects
  - Catalyst effects(1)
  - Heat of Reaction(1)
- Reaction mechanism
  - Product analysis(1)
  - Kinetic parameters(1)

(1)For selected compounds

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