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**Minutes of the
Tank Waste Science Panel Meeting
November 11-13, 1991**

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Preface

This document contains the minutes for the November 11-13, 1991 meeting of the Tank Waste Science Panel. The objective of this document is to provide an accurate recapitulation of the proceedings so that the diverse views of the Science Panel members can be documented. The content of this document has been reviewed by each of the Panel members to assure its accuracy. Editorial comments are clearly marked in the text and are provided only for clarification. Because of this philosophy, this document may contain provocative statements, opinions which may run counter to facts, facts which are presented out of the context of the tank chemistry and physics, and information that may later be shown as incorrect. These meeting minutes, like the previous minutes and those which will follow, are intended to chronicle the Science Panel activities and progress toward the understanding chemical and physical mechanisms that are taking place in the waste tanks at Hanford.

Summary

The sixth meeting of the Tank Waste Science Panel was held November 11-13, 1991, in Pasco and Richland, Washington. Participating scientists presented the results of recent work on various aspects of issues relating to the generation and release of gases from Tank 241-SY-101 and the presence of ferrocyanide in other tanks at Hanford.

The following important results were presented and discussed:

- Results from gas generation experiments at Westinghouse Hanford Company, with glycolate as the organic, indicate that the ratio of N_2O/H_2 gases closely approaches that found in Tank 241-SY-101.
- Laboratory experiments at Pacific Northwest Laboratory indicate that the organic complexants render the solid particles in simulated wastes hydrophobic so that gas bubbles adhere to the surface. This may play a part in the mechanism by which gases are retained in the nonconvective layer in Tank 101-SY waste.
- At Argonne National Laboratory, pre-irradiation of simulated waste solutions causes significantly enhanced gas generation at 60°C without radiation. This indicates that a reactive species is generated during radiolysis that could be an important species in the gas generation mechanism.
- Formaldehyde continues to be implicated as an important part of the H_2 gas generation in experiments carried out at Georgia Institute of Technology.
- In the ferrocyanide studies, ferrocyanide precipitates have been synthesized using the three known flow sheets used at Hanford. These materials are being characterized at Pacific Northwest Laboratory.

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Minutes of the Tank Waste Science Panel Meeting November 11-13, 1991

Introduction

The sixth meeting of the Tank Waste Science Panel was held in Pasco and Richland, Washington, at the Red Lion Inn (Pasco) and the Washington State University - Tri Cities Campus (Richland). During the first two days of the meeting, November 11 and 12, as in past meetings, participating scientists made presentations to the Science Panel. A session was held on the third day with a much broader audience that consisted of persons from the Department of Energy, Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL), and a limited number of public interest groups. The purpose of the open session was to disseminate information on the advancement in the understanding of the physical and chemical mechanisms for the generation, retention, and release of gases from Tank 241-SY-101. No summary of that session will be given here since the presentations given were nearly the same as those summarized below.

Three candidates for positions on the Science Panel were introduced. They were Professor Walter Klemperer from University of Illinois, Urbana, Illinois; Professor Glenn Russell from Iowa State University, Ames, Iowa; and Professor Graham Wallis from Dartmouth College, Hanover, New Hampshire.

The agenda for the three-day meeting is given in Appendix A. A list of the attendees for the first two days is shown in Appendix B; no attendance list was obtained for the third day of the meeting. In the following text, the presentations are summarized.

Day One of the Meeting

Further Analyses of the Tank Level Data

Tank waste level measurements are basically the only long-term historical measurements that are available for most of the Hanford waste tanks, including Tank 241-SY-101. These data have been analyzed by D. M. (Denis) Strachan in past Science Panel meeting reports. Recently, K. K. (Kevin) Anderson and Denis have more closely analyzed the data for slope changes to determine if the gas generation rate has been changing over the history of the tank. The results of this more careful analysis of the data are shown in Appendix C on page C.3. This figure indicates that the rate of gas generation has been fluctuating over the past 10 years, but there are no indications that the rate has been decreasing. There appears to be three periods during which the rate has increased. These increases are outside of the standard deviation of the data and so appear to be real. Interestingly, the third increase occurred when air lancing was being used in the tank and at nearly the same time that one would have predicted based on the two earlier increases. These data will be further analyzed to determine if there is a change in the frequency or magnitude of the gas release events as the rate is increasing/decreasing.

Denis and Kevin also looked for a correlation between atmospheric pressure changes and the onset of a gas release event. It had been qualitatively noted that a gas release event seemed to occur just after an

atmospheric low pressure has passed the area. As can be seen from the figures on pages C.5 to C.13, there is no correlation between the two phenomena. When the conditions are right for a gas release event, the event takes place.

An Estimation of the Gas Composition from the Waste in Tank 101-SY

Although several gas samples have been taken over the past year, the composition of the gases evolved from the waste remains uncertain. Because there are safety issues surrounding the composition of the gases being evolved from the waste and because the information is needed to support the work on the chemical mechanism, D. A. (Dan) Reynolds undertook the task of estimating the gas composition that most likely exists within the bubbles trapped in the waste (page D.2). The compositions used in the safety analyses have varied from equal quantities of H_2 , N_2 , and N_2O to 50% each of H_2 and N_2O . To date, gas compositions have been based on the results from the analyses of the vent line samples. More recently, samples have been taken through the in-tank sampling tubes located about 0.5 m above the surface of the waste. Samples taken from the vent line have been yielding gas compositions with a relatively constant N_2O/H_2 ratio (page D.3). Even though the sample analyzed using the on-line mass spectrometer and the in-tank sampling line yielded a different overall gas composition, the ratio of N_2O/H_2 was about the same as that from the samples obtained at the vent line (page D.3, data point to the lower left).

Results from the gas analyses performed at PNL using a gas mass spectrometer and at Idaho National Engineering Laboratory using a high precision mass spectrometer were analyzed by R. T. (Rudy) Allemann at PNL. The results from his analysis are shown on page D.4. These results, as well as previous results, did not include the quantities of water and ammonia that are known to exist in these gases.

Ammonia is known to exist in the gases released from the tank by three measurements: the organic vapor monitor that has been calibrated to measure NH_3 , Dragor Tube, and smell by the workers at the tank (page D.5). Dan integrated the response from the organic vapor monitor and the H_2 data to obtain an estimate of the total volume of the gases released in May 1991. This allowed him to estimate the ammonia content of the evolved gas.

To estimate the water content of the gas, Dan assumed that the gas was in equilibrium with the solution at the temperature of the waste (page D.6). Using the equilibrium and speciation computer code, ProChem (ULI Systems, Morris Plains, NJ), and the Gibbs-Duhem equation to estimate the water vapor pressure. Although the results from the on-line mass spectrometer measurements indicated the gas contained 18% H_2O , it is clear that the gas at the temperature of the tank could not sustain that quantity of water. The measurement must have been the result of a water drop entering the mass spectrometer.

The above techniques led Dan to estimate that the composition of the gas evolving from the waste is as shown on page D.7. This estimate indicates that gas evolved from the waste contains about 4% each of NH_3 and H_2O (page D.7).

Dan then discussed some of the reasons why results from the on-line mass spectrometer seem to be out of line with results obtained using the other analytical techniques (page D.8). Because both N_2O and CO_2 have molecular mass of 44, the N_2O quantity in the gas sample must be calculated. To obtain the composition of the evolving gases, the bulk gas is analyzed and the contribution from air is calculated from the Ar concentration. This technique leads to large errors in the calculated air contribution and, subsequently, the composition of the gas evolved from the waste. Using the Ar peak in the mass spectrum, Dan

estimated the gas composition (page D.9). However, Dan indicated that the fluctuations in the individual mass measurements were also quite large as shown on page D.10. These fluctuations combined with the uncertainty due to the fluctuations in the Ar mass peak make the estimating of the gas composition difficult.

In spite of these large uncertainties, Dan addressed the question of whether the mass 44 peak is due to N_2O or CO_2 . Dan looked at the variation in the mass peaks 2 (H_2), 28 (N_2), and 44 (page D.11). From these traces he was able to deduce that the gases giving rise to these peaks were originating from the tank waste. During a gas release event, Dan believes that the increase in pressure in the tank causes an increase in the flow rate and pressure of the gases in the sampling system for the mass spectrometer. This increase is often reflected in increases in the peaks corresponding to the constituent gases. Therefore, there are apparent increases at masses 28 and 32 (page D.12) that reflect this increase in pressure. In part, this conclusion is based on the results from the analyses of the grab samples in which the amount of O_2 believed to be coming from the waste is zero. If the gas giving rise to the mass 44 peak was due to CO_2 , then there should be evidence of the CO_2 fragment C. Dan looked for this mass in the spectra and could find none (page D.13). The Ar response shown on page D.13 exemplifies the problem with using Ar as the tie element when calculating the composition of the gas coming from the waste. Further evidence that the mass 44 peak is due to N_2O is found in the response at mass 30 (NO ; an ionization fragment of N_2O). As shown on page D.14, the response to the increase in the gas release is the same at mass 30 and 44. It is concluded that the response at mass 44 is due to N_2O . During a gas release event, the correspondence between the peaks at mass 44 and 30 is excellent; a straight line of unit slope results when the data are plotted together (page D.15). The data lying near zero slope are the data taken away from the gas release event.

Nitrogen release during the gas release event is indicated by increases in the ratio of N_2/Ar during the event, whereas the O_2/Ar does not increase (page D.16). Likewise, water appears to be a constituent of the gas mixture released from the waste as Dan estimated (page D.17). The peak prior to the gas release event is due to an increase in the atmospheric moisture during a rain storm on May 16. The figures on pages D.18 and D.19 show the mass spectrometer responses at masses 28 and 32, respectively.

Dan concluded that the gas mixture is indeed flammable, but there are some diluents to mitigate the danger (page D.20). A better gas monitoring strategy is needed to make the results from the various methods of analysis consistent.

During the discussion, it was pointed out that there are some light molecular weight organics with masses close to those of CO_2 , N_2O , etc. Dan pointed out that there have been separate analyses for volatile organics and none have been detected. Analyses of the grab samples using the high resolution mass spectrometer at the Idaho National Engineering Laboratory did not reveal any light molecular weight organics, thereby suggesting their absence. Cryogenic samples were taken quite some time ago, but results from the analyses of these samples have not been made available.

In the past there has been some concern that there is a leak in the sampling system on the vent line. A leak could explain the differences seen between the mass spectrometer and the grab samples at the vent line.

There was some discussion about the possibility that the waste was stratified such that the gas generation was not uniform. It was noted that the Na and ^{137}Cs were more-or-less uniform between the top

layer and the bottom layer of the tank. Preliminary information, however, suggested that there was quite a large amount of variability in the ^{137}Cs results from the samples taken from the convecting layer. Also noted was the very high quantity of Cr in this waste. For the material in the nonconvecting layer, the Cr was about 10 times higher than the Fe - about 0.7 wt%. Dan indicated that results from earlier analyses of the waste in Tank 241-SY-103 also indicated similar high Cr concentrations.

Gas Generation Studies at Westinghouse Hanford Company

D. L. (Dan) Herting could not attend the meeting, but Dan Reynolds presented the results from the laboratory studies of gas generation. Dan Herting has been measuring the rate at which gases are generated in synthetic waste and the composition of the evolved gases in order to gain experience with the apparatus that will shortly be used to measure the gas generation rate and composition of the gases from a composite sample of the last core sample taken from the tank. Some problems exist with the apparatus as noted at the last meeting. Dan Reynolds highlighted additional experimental problems.

Four duplicate experiments were performed and the results are shown on page E.2. Of the four experiments, only two, Runs 12 and 13, seemed reproducible. In Run 11, the longest, some difficulty was experienced in sampling the gas at about 2600 h. This apparently allowed some air to enter the apparatus and cause an increase in the rate. Even though these experiments were started with air present, the pressure in the apparatus varies from about 400 torr to 700 torr. A similar increase in the rate of gas generation can be seen at about 600 h for Run 13 and 1400 h for Run 12.

Two experiments were performed with glycolate as the organic in the simulated waste mixture. In one experiment the cover gas was air (Run 17) and in the other it was He (Run 18). Under both cover gases, the glycolate-containing simulated waste generated gas. Under He the rate was initially faster but decreased to the same rate as with the air cover gas at about 1200 h. It is uncertain what is taking place to cause these variations in rate. At Georgia Tech, the rate of gas generation is found to be the same under air or He.

Dan Herting has also measured the composition of the gases being evolved from these simulated wastes. The results from these analyses are shown on page E.4. Dan Reynolds cautioned that the values shown have a great deal of uncertainty ($\pm 25\%$) to them, but his attempt was to see if the average values gave some indication of differences. It is interesting to note that the glycolate-containing simulated waste solutions generated gases with about the same $\text{N}_2\text{O}/\text{H}_2$ ratio as has been observed in the gases evolved from Tank 101-SY.

The results from Dan Herting's experiments sparked a spirited discussion. Most of the Science Panel indicated that the design of the experimental apparatus needed to be reviewed. It is important that the results from the experiments with the actual waste are reliable so that the results can be compared with the results from the experiments being carried out at Georgia Tech and Argonne National Laboratory. The fact that duplicate runs do not yield reproducible data suggests that this comparison will not be reliable. It was strongly suggested that Dan Herting contact N. E. (Ned) Bibler at Westinghouse Savannah River Site to determine the applicability of using an apparatus of similar design to the one currently in use to continuously measure the generation of H_2 during the treatment of waste sludges with formate.

Dan Herting plans to obtain gas generation rate data at 25°C and at 60°C to get an estimate of the activation energy for the decomposition of the organic in simulated Tank 101-SY waste. On an Arrhenius plot prepared at Georgia Tech, a change in mechanism is noted in the range of 50°C to 60°C.

A discussion was held about the contribution that noble metals could be playing in the generation of the gases in Tank 101-SY. Noble metals have been implicated in the generation of H₂ during the treatment of Savannah River Plant sludges with formic acid. Without the noble metals present, no or little H₂ is formed. The waste sludges contain the noble metals as a result of the fission process. Although the analysis of the noble metals is difficult, recent progress has been made in the Hanford Waste Vitrification Project at PNL. At Savannah River, the waste sludges have been analyzed quite thoroughly with the result that the radionuclide and trace element content of the sludges accurately reflects the fission yield curves for the isotopes. Analyzing some other, more easily measurable isotope may provide some indirect measure of the noble metal content of the sludges in Tank 101-SY.

It was suggested that the most reactive species in the system might be expected to have the lowest concentration. It was pointed out that in the Argonne National Laboratory presentation to be made later, it will be seen that radiation produces a relatively reactive species at 60°C that is relatively unreactive at room temperature.

At the end of the discussion, it was strongly recommended that Dan change the apparatus he is using to a flow-through design. For the reasons pointed out above, these experiments need to be performed correctly so that the results can be reliably compared with the results from the tests with simulated waste.

Synthetic Waste Studies at the Pacific Northwest Laboratory

Two tasks are being funded at PNL through WHC (page F.2) - Chemo-Physical Studies of Gas Retention and Integrated Testing. The results from these studies were presented by S. A. (Sam) Bryan.

Since heating of the waste is one of the mitigation options and most of the experiments are performed at elevated temperatures, it is important to know how the physical properties of the simulated waste changes with temperature. The figure on page F.3 is an indication of the variation in the solution density with increasing temperature. Most of the density change occurs because the solubility of the solids increases with increasing temperature. The experiment was actually performed by heating the solution and solids that result from using Dan Herting's recipe (but without organics) to about 110°C. At 110°C, no solids are present; solids appear at about 80°C. As the solution is cooled, any solids that form settle to the bottom of the container. A sample of the supernatant liquid of known volume is removed and weighed at room temperature. The density is calculated. There is a rapid change in the density of the liquid phase over the temperature range of 45°C to 55°C. If the density of the resulting liquid at the elevated temperature in the nonconvecting layer in Tank 101-SY behaves similarly and the resulting density is greater than the liquid density of the convecting layer, heating of the waste will not promote waste mixing. Release of the gas, however, may still occur.

In an attempt to demonstrate that N₂O can be transported through the liquid layer because of the high solubility of N₂O in the aqueous phase, an experiment was performed to show the rate at which the gas was transported and the effect of varying the partial pressure of N₂O (page F.4). It has been suggested that a possible explanation for the discrepancy between the N₂O/H₂ ratio measured in the laboratory and in the tank would be some mechanism by which N₂O is preferentially released from the nonconvecting

layer over the H_2 . In this experiment, a buret was filled with the gas/gas mixture and connected to a piece of tubing containing water. The volume of the gas in the buret at constant temperature and pressure was measured. Since the data fall on a straight line on a plot of the volume of gas versus time, the rate is not governed by diffusion. The results from this experiment are very preliminary because the data had been obtained only recently and the conditions of the test not thoroughly thought through. Nevertheless, the results came under a fair degree of criticism by the Science Panel members who questioned the need for these tests. In general, the Science Panel members felt that the N_2O gas was dissolving in the aqueous phase rather than being transported through the liquid. Even if the gas was being transported, the transport would be expected to be accelerated due to micro convection currents in the tubing.

One of the postulated mechanisms by which gases are retained in the nonconvecting layer in the tank is that the organics sorb on the surface of the solid particles in the tank and thereby create a layer that is slightly hydrophobic. A measure of the hydrophobic nature of a surface is the contact angle (page F.5). As the contact angle between a gas and the liquid increases for any solid material, the harder it will be to remove a bubble from that surface, hence large retention of gases. Since the contact angle is inversely dependent on the surface tension of the liquid at the liquid-vapor interface (σ_{LV} on page F.5) and since this property can be measured independently, the effect of electrolyte concentration and temperature on surface tension was investigated. Surface tension varies differently for each solution with increasing electrolyte concentration (page F.6). The variation in the measured surface tension for distilled water and simulated waste is shown on page F.7. Over the temperature range found in Tank 101-SY (up to 333 K), the surface tension of the simulated waste does not change significantly.

Schematically, the interaction of gas bubbles with surfaces that are hydrophobic or wettable is shown on page F.8. Ideally, one would like to measure the contact angle using the materials of interest, in this case $NaNO_3$, $NaNO_2$, $NaAlO_2$, Na_2CO_3 , and simulated waste solution. However, it is impractical to perform these studies with any of the mentioned solids because flat surfaces are needed. For these measurements, the instrument consists of a light source, an optically flat plate of sapphire, and a lens fitted with a goniometer. In the sapphire plate, a small hole is drilled through which gas can be injected into the liquid lying on the plate to form a bubble. The results from these measurements are shown on page F.9. These data indicate that the two organic chelators EDTA and HEDTA increase the contact angle of the gas on the surface of the sapphire plate with increasing organic concentration. Pictures of the waste taken from the tank show solids with small bubbles adhering to the surface.

Integrated tests have been carried out at PNL in an attempt to confirm the results being obtained at Georgia Tech and Argonne National Laboratory. The results from the radiolysis experiments at $6 \cdot 10^5$ R/h with and without HEDTA present at $90^\circ C$ and without a radiation source are shown on page F.11. The radiation dose rate in these experiments is about 300 times higher than the estimated dose rate in the waste in Tank 101-SY. These results indicate a linear increase in the gas generated over 120 h with no apparent induction period. At the radiation conditions of this test, the radiolysis contribution to the gas generation completely dominates the generation by purely thermal effects, but the rate of generation is still constant. In the absence of a radiation source, the effect of changing the organic concentration is clearly seen - changing the organic concentration by a factor of two changes the rate by a factor of two.

After 120 h, the gas was sampled for analysis. The results from these analyses are shown on page F.12. These results confirm those obtained at Argonne National Laboratory where they find that

under γ -radiolysis the generation rate of N_2O is increased. No increase in the N generation rate is found when the samples are irradiated and the rate of H_2 generation is increased in the presence of radiation.

Using the available data, the contribution to the overall gas generation in Tank 101-SY was estimated and compared with the observed generation rates (page F.13). Results from the generation of N_2O are much higher than those estimated from the gases released from the tank. Sam estimated the contribution to the H_2 generation due to steel corrosion using the published corrosion allowance (Mackey and Divine 1986). This estimate does not presuppose that this is the main gas being evolved during corrosion; the gas composition was not measured by Mackey and Divine (1986). It is generally supposed that the tanks are passively protected by the waste that is placed in them. However, there is a region at high pH where corrosion can take place under reduced oxygen fugacity (page F.14). So long as there is a moderate amount of O_2 present, the metal will be passively protected. However, the data from Argonne National Laboratory suggests that free O_2 is rapidly removed from the system when organics and radiolysis are present in simulated waste.

Because the composition of the gases generated during the steel corrosion studies of Mackey and Divine (1986) and because the Pourbaix diagram is for simple NaOH solutions, Sam performed an accelerated scouting test to determine what gases, if any, were generated during corrosion of steel. The results of these experiments are shown on page F.15. When simulated waste containing 0.35 M HEDTA is mixed with Fe at 90°C under an Ar/20% O_2 atmosphere, more gas is generated than without the HEDTA. The identity of the gases is shown on page F.16. Based on these very preliminary results, H_2 appears to be a product of the corrosion of steel. It is uncertain if corrosion of the mild steel that is used to construct the tanks will yield the same results and if the gas yield is quantitative.

Some of the conclusions drawn by Sam from his results caused a lot of discussion. The Science Panel members were concerned that the steel corrosion results might be misconstrued as meaning that all of the Hanford tanks are corroding. It is important to recognize that these results are based on the maximum allowance for corrosion in the Hanford tanks and that corrosion quantitatively yields H_2 . There is no reason to suspect that the tanks are corroding at the maximum allowable rate nor that the reaction is quantitative. The Science Panel members felt that some of the conclusions derived from the results presented at the meeting were based on too few data. Some of the experiments were being performed at Georgia Tech and Argonne National Laboratory, so duplicating them at PNL was perhaps premature. There are some differences between the laboratories and that might justify additional testing of this type.

One of the attendees observed that there are three laboratories performing tests and there are as many different temperatures being used in the experiments. More consistency is needed among the laboratories so that the results are more comparable. There may be good reasons for the selection of the various temperatures but perhaps there could be a consensus about what temperature(s) to use.

Summary of Results from Argonne National Laboratory

At Argonne National Laboratory a group of researchers headed by D. (Dani) Meisel is performing research on the effects of radiolysis on the chemistry of gas generation in simulated Tank 101-SY waste (page G.1). Dani pointed out that at the Nuclear Research Center Jülich laboratory in Jülich, Germany, radiolytic sources of H_2 and N_2O have been observed (page G.2). Dani briefly reviewed the potential sources of gases from the Hanford waste systems (pages G.3 through G.5). Since little is known about the mechanism by which the organic molecules interact with the many reactions that take place in the aqueous

nitrate/nitrite system, Dani performed calculations at various values of the product of the rate constant, k , for the hydrogen abstraction reaction ($\text{RH} + \text{H} \rightarrow \text{R} + \text{H}_2$) and the concentration, c , of the organic (RH), see page G.6. This set of calculations yields bounding values for the product, since an estimate of the net $G(\text{H}_2)$ value is known from the observation of H_2 generation in the tank and the H_2 generation in laboratory experiments. The effect on the yield of H_2 of the large and small spurs and the concentration of NO_3^- and NO_2^- is shown on pages G.7 and G.8, respectively. One of the conclusions from these results is that it is unlikely that a chemical additive will be more efficient at scavenging H_2 precursors than NO_3^- and NO_2^- which are present at ample concentrations. Although somewhat speculative, calculations can be made of the effect of the product of the rate constant for the abstraction reaction and the concentration of RH on the H_2 yield (page G.9).

Turning to the results from their experiments, Dani showed the observed yields of H_2 and O_2 in the absence of the organics (page G.10). In the presence of any of the organics, the $G(\text{O}_2)$ becomes negative, i.e., O_2 is destroyed. In radiolysis experiments, it is useful to operate at a high dose rate so that the time to obtain results is minimized. This requires that one demonstrate there is no dependence of the G value on the dose rate. For this system, Dani has shown the $G(\text{H}_2)$ is insensitive to the dose rate (page G.11). There is, however, a dependence on the amount and type of organic present (page G.12) and an empirical dependence on the number of carbon-hydrogen or nitrogen-hydrogen bonds in the molecule (page G.13). The "Efficiency" shown in the figure on page G.13 is the slope of the lines shown in the graphs on page G.12. There is no theoretical basis for this observation; it is just an empirical observation.

One can obtain the overall value for the reaction rate constant for the abstraction of hydrogen from the organic. Therefore, a reaction rate constant can be obtained by fitting observed $G(\text{H}_2)$ at various concentrations of organic (pages G.14 and G.15). Using this technique, Dani was able to obtain estimates for the rate constants and the activation energies shown on page G.16. To show the difference between the rate of H_2 generation at high pH and low pH, Dani listed known rate constants for the abstraction reaction at 25°C and a pH of 1 (page G.16).

Dani noted that the correlation between the estimated rate constants and the empirical "efficiency" R values (slopes on G.12) was also good (page G.17).

As in previous laboratory work, the rate at which N_2O is generated is much higher than the rate at which H_2 is generated. This trend appears also to be the case in the radiolysis experiments summarized on page G.18. The rate of N_2O generation is about 10 times higher than the H_2 generation. These experiments have been performed at various concentrations of organic and at various dose rates and doses (page G.19). From this table, it can be seen that the $G(\text{N}_2\text{O})$ is relatively insensitive to the dose and to the concentration of the organic, but sensitive to the dose rate. Nitrous oxide is generated in these solutions only when the organic is present; N_2O is not found in the list of radiolytically generated species from the calculations that were performed in the absence of organics.

The effect of temperature on the $G(\text{H}_2)$ and $G(\text{N}_2\text{O})$ is significant (page G.20). More significant, however, is the effect of preirradiation on the thermal generation of both H_2 and N_2O . On several samples that had been irradiated, the thermal production of H_2 and N_2O was checked. Relative to similarly treated samples without preirradiation, the rate of generation was about 10 times higher (pages G.21 and G.22). The fact that the samples had been stored at room temperature for several weeks before being tested, suggests that there is a radiolysis product that is chemically quite stable at room temperature, but reacts quite readily at elevated temperature.

Dani speculated the pathway by which several of the organics identified in 1986 by Lokken et al. (1986) and in the work being carried out at Georgia Tech could be generated (page G.23). This scheme leads to formaldehyde, which is suspected of being the most rapidly reacting species in these systems and which appears to be a radiolysis product.

Some of the products of the direct interaction of the radiation on these solutions are shown at the bottom of page G.24, while the result of the ex-spur reactions are shown at the top of the page. Some of these species have been implicated as being important in the reaction schemes proposed by the group at Georgia Tech and from the work of D. D. Siemer at Westinghouse Idaho Nuclear Company.

The results from the work at Argonne National Laboratory is summarized on pages G.25 and G.26.

Summary of Results from Georgia Institute of Technology

The group (page H.1) led by E. C. (Gene) Ashby has made significant strides toward understanding the mechanism by which gases are generated in simulated Tank 101-SY waste. Based on the results to date, the group at Georgia Tech proposes the set of reactions shown on page H.2 as the set of reactions that can be used to explain the gases generated during the decomposition of glycolate in simulated waste. Evidence exists for many of these reactions; further evidence will be needed to confirm some steps in the mechanism. Steps 8 and 9 (page H.2) are not known, but are proposed as methods of generating N_2 from the available chemicals in the system.

Gene listed the key results along with the experiments that backup the key conclusions (pages H.3 through H.5). As noted in previous meetings, an induction period exists that may be as long as 70 h (item 1, page H.3). The results from Experiment A34 are plotted on page H.6. This induction period persisted even though the mixture was stirred (item 5, page H.3). This is counter to Duane Siemer's observations; he did not observe an induction period for any of the solutions or organics tested, so long as the organic yielded H_2 . However, Duane Siemer used a purge gas that was bubbled through the test solution. That operational difference in his experiments may be the explanation for no induction period.

Also noted in earlier meetings and in earlier experiments by Delegard (1981), no gases were evolved from solutions containing no organics (item 2 on page H.3 and plotted on page H.7). No gas was evolved during experiments with EDTA under air or Ar atmospheres (item 3 on page H.3 and plotted on pages H.8 and H.9). This result was also noted in earlier experiments. With HEDTA as the organic species in solution, gas was evolved at 0.21 mL/h and 0.39 mL/h under a He and air atmosphere, respectively (item 4 on page H.3 and plotted on pages H.10 and H.11). This runs counter to some of the earlier experiments in which the experimenters reported no gas evolution in the absence of air.

The use of ultrasound has been proposed as a method for mitigating the episodic release of gases from Tank 101-SY. In a scouting test to determine the gross effects of ultrasound on the chemistry of gas generation in simulated waste, a gas generation experiment in the presence of ultrasound was performed. The results (page H.4, item 6 and plotted on pages H.12 and H.13) indicate that the gas generation rate is slower, but more erratic.

With glycolate as the organic species, no difference was noted between the gas generation rate in He or air (page H.4, item 7 and plotted on pages H.14 and H.15). The gas generation rate was measured at 0.34 mL/h. However, when Al was eliminated from the waste formulation, no gases were evolved

(page H.4, item 8 and plotted on page H.16). Elimination of NO_2 from the simulated waste reduced the gas evolution to about 20 mL of gas in over 400 h of the experiment (page H.4, item 9, plotted on page H.17). Elimination of the NO_3 from the simulated waste formulation did little to reduce the rate of gas evolution (page H.5, item 10 and plotted on page H.18). This implies that NO_2 plays the dominant role in the mechanism for the thermal generation of gases in this system.

There has been a question concerning the role of the trace elements in the mechanism of gas generation. One of the transition metals that could play an important role in gas generation is Cr. Chromium was added to the simulated waste samples at the several parts-per-million level. Both Cr(III) and Cr(VI) were used. In the absence of air, the generation rate of gas increased to 0.5 mL/h from 0.34 mL/h when glycolate was the organic present (page H.5, item 11 and plotted on page H.19). In the presence of air, the rate decreased to 0.13 mL/h from 0.34 mL/h (page H.5, item 11 and plotted on page H.20).

In an effort to rapidly analyze the products from the experiments carried out at Georgia Tech, ^{13}C nuclear magnetic resonance (NMR) has been selected as one of the analytical tools. A ^{13}C NMR data base is being developed (page H.21). The results for HEDTA and glycolate are shown on pages H.22 and H.23, respectively. In both cases, benzene is used as a standard and has NMR peaks at about 130 ppm in the spectra shown on pages H.22 and H.23. For both HEDTA and glycolate, formate is found as a product of the reaction. Carbonate is present in abundance in the waste formulation. However, CO_3^{2-} generated from ^{13}C -labeled HEDTA would contain ^{13}C -enriched CO_3^{2-} . This increase would be detectable using NMR.

Most of the evidence from the experiments that have been performed to date suggest that formaldehyde (HCHO) plays an important role. Gene and his coworkers have been performing experiments to elucidate that role. Part of the reaction that takes place for formaldehyde in strongly alkaline solutions is the Cannizzaro reaction (page H.24). In this reaction, the end products are, for formaldehyde, methyl alcohol and formate; in general the alcohol and the carboxylate anion are formed. The Cannizzaro intermediate (shown as "1" at the bottom of page H.24), if it could be detected, would be proof that this reaction was taking place. Evidence for this intermediate exists in the spectra taken at Georgia Tech and in the experiments performed with $\text{D}_2\text{O}/\text{OD}^-$ (page H.25). The spectral evidence is in the shift and broadening of the peaks. The presence of oxidizing agents such as Cu(I) or H_2O_2 can be used to verify the presence of the Cannizzaro intermediate (page H.26). As the results for the experiments with H_2O_2 suggest, when sufficient oxidizing agent is present, the reaction product is entirely formate instead of formate and methyl alcohol. Hydrogen peroxide, generated in the tank by radiolysis, reacts with the Cannizzaro intermediate to form a free radical and, subsequently, a free radical coupling product shown at the bottom of page H.27. This coupling product decomposes to H_2 and formate. Evidence for the presence of the free radical comes from experiments with Cr(III) (page H.28), which does not increase the rate or amount of gas generated. Addition of Cu(II) causes an increase in the amount of gas generated (page H.29). The reactions shown at the bottom of page H.29 show how the reaction with Cu(II) generate the same free radical and coupling product as did H_2O_2 . The presence of O_2 (page H.30) or p-hydroquinone (page H.31) also decreases the amount of H_2 from formaldehyde, suggesting the presence of a free radical intermediate. Increasing the temperature or the concentration of OH^- increases the yield of H_2 (page H.32).

To further substantiate the reactions shown on the previous pages, experiments were carried out in $\text{D}_2\text{O}/\text{OD}^-$. The results of these experiments are tabulated on page H.33. It was known from the last

meeting that there is a measurable exchange between H_2 and D_2O . Experiments were performed to demonstrate that while the effect is measurable, the contribution to the results is predictable. At temperatures below $90^\circ C$, the results indicate that both hydrogens are coming from the formaldehyde. Hence, the need for a species such as the condensate shown on previous pages. At $90^\circ C$, the mechanism has changed such that the predominant product is D_2 which could only come from the D_2O . This reaction is dramatically different from the reaction that yields H_2 at the lower temperatures.

Other aldehydes have been tested to help elucidate the mechanism of H_2 generation (page H.34). Pivaldehyde should yield H_2 gas when tested.

To recap, the reactions starting with formaldehyde to yield H_2 and formate are shown on page H.35. The last step in the mechanism is probably the most controversial. An alternative route was suggested by one of the panel members. The molecule that precedes the formation of H_2 could be unstable relative to the formation of H_2 and CO_2 , which in alkaline solution would yield CO_3^{2-} . A good test for the proposed reaction is to use a ratio of deuterated and non-deuterated formaldehyde in D_2O/OD^- . If the proposed reaction is correct, then one should see HD, D_2 , and H_2 as the reaction products. However, if the breakup of the organic precursor to H_2 and CO_2 is correct, then a mixture of deuterated and non-deuterated formaldehyde should yield a mixture of H_2 and D_2 .

Experiments carried out using ^{13}C -labeled HEDTA and glycolate yielded the results shown on pages H.36 and H.37 and by the spectra shown on pages H.38 through H.43. In these experiments, because the hydroxyethyl carbons in HEDTA are enriched in ^{13}C , it can be determined that the organic is the source of the CO_3^{2-} .

The N chemistry in this system is somewhat unusual in that all oxidation states of N are found in the N-containing products. Therefore, a literature search was performed to become more familiar with N chemistry (page H.44). Reduction of NO_2^- can yield N_2O and NH_3 as products (page H.45). Three reaction intermediates have been identified in the literature with lifetimes long enough that they might play a role in the waste chemistry, if formed (page H.46). Based on the literature, it is suggested that NO^- and $N_2O_2^{2-}$ may be intermediates and that a possible route to N_2 is by reaction of NO_2^- and $N_2O_2^{2-}$ (page H.47). Another possibility is that H_2NO^- is formed (page H.48) which can lead to N_2 and N_2O . It should be noted that the group at Argonne National laboratory has performed experiments with ^{15}N and found that the sole source for N_2O is inorganic N, i.e. NO_2^- or NO_3^- .

Two methods have been selected for the analysis of anions - Ion Chromatography and Ultra-violet spectrophotometry (page H.49). The results shown on page H.50 show that there is consistency between methods.

Organic Analytical Methods Development and Preliminary Data for Tank 101-SY

At PNL, methods are being developed by J. A. (Jim) Campbell for determining the quantity of the organic species in the waste contained in Tank 101-SY. The material was presented by R. M. (Roger) Bean. Roger's talk was divided into the topics shown on page (I.2).

As recognized by the Science Panel members, there is a need to determine the organics that are present in Tank 101-SY as confirmation for any chemical model that will result from the studies at Argonne National Laboratory, Georgia Tech, WHC, and PNL (page I.3). Also, because of the

uncertainties associated with the safety of the waste and with remediation and mitigation of the safety issues, there is a need to know what organics are contained in the waste. The measure of how good the analyses have been is the agreement between the analyzed total organic carbon and the calculated organic carbon based on the analyzed organic species in the waste. Methods to analyze for two major categories of organics have been developed or are under development (page I.4). The two major categories are peroxides and chelators. Methods to identify other organic species have not yet been initiated. A systematic approach is needed since safety issues are causing pressure to develop a remediation/mitigation technique.

There was an early emphasis on the chelators because of the knowledge of the process chemistry at Hanford and because this class of organics is generally water soluble (page I.5). These same species can enhance transport of radionuclides through the soil in the event of a leak. The chelators of interest and some of the degradation products are shown on page I.6.

Four methods are being investigated for the analysis of chelators and chelator fragments (page I.7). Within the derivitization category, five techniques have been investigated (page I.8). The BF_3 /methanol method was used for the analyses performed in 1986 and reported in Lokken et al. (1986). It has been found that this method of derivitization yields other compounds than just the methyl esters of the parent carboxylate. One of the reaction products is the CO_2CH_3 (lactone) shown on page I.9. Although BF_3 is not considered the ideal agent for derivitizing the water soluble organic acids, it is the best of the five listed (page I.10). In general, there are disadvantages to derivitization (page I.11), but in some cases this technique is needed to separate the organics from the highly radioactive portion of the waste.

High performance liquid chromatography (HPLC) has been investigated for use in analyzing the chelators in the waste (page I.12). It was suggested quite early in the investigation that the Science Panel contact a scientist at W. R. Grace, one of the largest producers of chelator chemicals. The method used at that company was found to be unacceptable for use on the waste solutions. The method was modified such that the mobile phase in the HPLC contained no Cu. Chromatograms showing the results from using the W. R. Grace and the PNL methods are shown on pages I.13 and I.14, respectively. One of the main problems to be worked out is the cleanup of the simulated and actual waste materials before analysis to remove interferences (page I.15).

Liquid chromatography coupled to mass spectroscopy (LS/MS) is also being investigated as an organic analysis tool (page I.16). To overcome the mobile phase incompatibility with the mass spectrometer interfaces, a reverse phase ion exchange column has been employed. Two mass spectrometer interfaces have been investigated--particle beam and thermospray. Each of the interfaces have advantages, but thermospray appears to be better suited to the types of solutions that will be analyzed in this program. Examples of the spectra that have been obtained with standard solutions of HEDTA, EDTA, ED3A, and citric acid are shown on pages I.17 through I.22. Coupling the LC/MS to an ICP/MS will allow identification of both the organic moiety and the metal to which it is complexed. The conclusions of the organic analytical methods development task are listed on page I.23.

Samples of the crust in Tank 101-SY were sent to PNL from WHC for analysis of the organic fraction. Two methods have been attempted in the analysis of these samples. In one method, the material has been dissolved in acid and then the organics have been derivitized. In the second method, as much of the crust material as would have been dissolved in water and then the organic material derivitized. It is believed that the bulk of the organics are water soluble and even though all of the solids do not dissolve in

water, the organics would dissolve. Results from the acid dissolution of the crust material are shown on page I.25. Methylamminoiminodiacetic acid (MAIDA) is an uncertain assignment. The compound giving rise to this peak appears to be the result of the sample preparation, at least in part. Acid preparations of the standard solutions of HEDTA also give rise to a peak at this position. In the water-treated crust sample, MAIDA is also found (page I.27). The material that eluted at about 10 minutes and was assigned to citric acid was analyzed in an infrared spectrometer and the spectrum compared with the spectra stored in a library (page I.28). The compound was determined to be the trimethyl ester of citric acid. By comparison, the spectrum shown on page I.26 is less complex than the spectrum shown on page I.29 that resulted from the analysis of the liquid sample from Tank 107-AN (Lokken et al. 1986). The analysis of the crust sample recovered about 10% to 20% of the total organic carbon.

Several persons at the meeting suggested that instead of analyzing the crust samples, the samples from the convecting and nonconvecting layers needed more attention. With the knowledge we have now, it seems prudent to be looking for low molecular weight organics such as glycolate, formate, formaldehyde, acetate, etc. These materials may be too volatile to be quantitatively recovered during the sample preparation steps.

For reference purposes, many spectra are included in the viewgraph package but without comment or discussion.

Summary of Physical Modeling at Westinghouse Hanford Company

Both physical and numerical modeling activities are being carried out at WHC. Results from these efforts were summarized by T. M. (Tom) Burke (page J.1). Modeling, both physical and numerical, is needed to demonstrate that a remediation/mitigation strategy can be carried out effectively and safely (page J.3). Understanding the rollover phenomenon in the tank is important from the stand point that it results in a partial verification of the physical mechanism and physical properties of the waste. These physical properties form the bases of the physical and numerical models. Physical and numerical modeling is being carried out at PNL and WHC in a team approach (page J.4). Two physical models are being pursued in a complementary team effort.

At WHC, physical modeling is being pursued through the use of dynamic simulants (page J.4 and J.6). These simulants allow one to vary the physical properties in order to determine the conditions under which the gases are retained and released in the tank. Finding a dynamic simulant may be logistically important since a very large volume of simulated waste may present a disposal problem. Early examples of dynamic simulants included the yeast-corn meal-starch model presented at the last meeting in Atlanta (page J.7). Current methods of generating gases within the simulated waste include pressurization with CO_2 followed by a decrease in pressure to effect supersaturation within the aqueous phase and decomposition of NaHCO_3 . Using these dynamic simulants, gas retention and thermal inversions have been observed (page J.8). For instance, with NaHCO_3 gases released in the lower layer attach to particles which then rise to the surface. The solid-gas mixture remains at the surface while the gases are released. However, more work is needed and is continuing (page J.9).

In the area of numerical modeling, the staff at WHC have been using the FATHOMS/GOTHIC (NAI 1987) code (page J.10). This code has been modified and includes a viscosity model in which the viscosity increases with increasing particle density. The physical properties that were used as input to the

FATHOMS/GOTHIC code were selected based on existing data from the tank and data from other sources (page J.11). Most of the values are reasonably close to the values for the physical data obtained from actual Tank 101-SY samples.

Tom showed a video tape of a simulation. The figures on pages J.12 and J.13 illustrate the output of the FATHOMS/GOTHIC code. In this simulation, a lot of solids are needed to attain the high solid/liquid viscosity needed for a rollover. About 23 vol% gas was needed to get the buoyancy to raise the particles, but 28 vol% was used in the simulation presented. Spherical particles were used. During the rollover, gases are released and it is possible to calculate the gas flow in the tank plenum space. The results of this calculation are shown on page J.14. The calculated values (symbols) are compared with the measured values from the October 1990 event (solid line). The calculations yield a gas release in which the flow rate increases more slowly than observed and does not predict as high a maximum flow rate as observed. The agreement is quite good considering the lack of specific information on the physical properties of the waste. During the calculation, the thermal profile can also be simulated. The comparison between the calculated values and the observed thermal profile is shown on page J.15.

These calculations suggest that perhaps as much as 50% of the gas is retained in the tank after a gas release event (page J.16). This result is in agreement with some of the calculations performed at PNL and discussed later by R. T. Allemann. As indicated above, more work is needed to validate the model and these conclusions (page J.17).

One of the uses of numerical models is the prediction of future actions that might be taken in the tank such as mitigation or remediation, but physical models are also needed to validate the calculations (page J.19). Several concepts are being considered, one of which is mixing (page J.20). The physical models allow one to quickly vary the conditions being tested and test various designs for the pumps and jets that would be used to stir the waste. A physical model of the tank has been constructed from lucite (page J.21). There are several advantages of using of a 30' sector model of the tank; one disadvantage is the possibility of wall effects. Numerical modeling of the mixing concepts is being carried out at PNL using the TEMPEST code (Trent and Eyer 1990) (page J.22). Some of the staff at WHC are becoming familiar with the use and capabilities of the TEMPEST code. Numerical modeling of mitigation by mixing will likely be done using both codes since independent confirmation of the results may be needed to obtain permission to install a remediation/mitigation technique in Tank 101-SY.

Day Two of the Meeting^(a)

Ultrasound Slurry Degassing for Mitigation of Tank 101-SY

Probably the most controversial mitigation technique is the use of ultrasound to "shake" the bubbles loose from the nonconvecting layer. This technique was proposed by the scientists at Los Alamos National Laboratory and presented by S. F. (Steve) Agnew. Steve summarized the current understanding of the composition of the waste and the nature of the layers within Tank 101-SY (pages K.2 and K.3). Since the gases in the nonconvecting layer are thought to adhere to the surfaces of the solid particles in that layer and ultrasound has been used in industry to defoam process solutions and slurries, ultrasound might be

(a) The presentations on the first day were longer than anticipated, so the last two talks scheduled for the first day were presented on the second day.

useful in removing the bubbles from the nonconvecting layer. This is accomplished by causing the adhering bubble to oscillate by exciting one of the monopole frequencies of the bubble (page K.4). This process may require ultrasound at about 1 MHz and 10 mW of power. This energy and frequency would be appropriate for bubbles about 1 μm in diameter (page K.5).

Bubbles in the nonconvecting layer are believed to form when the gases being chemically and radiochemically generated reach saturation and nucleate on the surface of the solid particles (page K.6). Application of ultrasound will cause the bubbles to oscillate sufficiently to break away from the solid surface. These bubbles will then be transported to the nodes and antinodes of the ultrasound radiation (page K.7). Transport occurs because the ultrasound waves represent pressure surges to which the bubbles respond by moving (page K.8). These bubbles will coalesce into larger bubbles which will then float to the surface.

At Los Alamos, tests are being carried out to define the power and frequency requirements for the ultrasound instrument that would be placed in the tank (page K.9). An instrumented tank has been constructed and simulated waste has been studied. One of the efforts that is needed is to have a simulated waste that undergoes swelling and gas release. This is needed to accurately test the ultrasound technique (page K.10). A schematic of the instrumented tank that Steve has constructed is shown on page K.11. The dimensions of the waste tank are to scale and the waste layers are scaled accordingly (although layer thicknesses from Tank 101-SY are shown). Steve uses a coil heater in the bottom layer to generate the thermal profile exhibited in the nonconvecting layer of Tank 101-SY (page K.12).

The simulated waste that Steve has been using (page K.13) is different from the composition others in the program are using. This may be somewhat of a problem since the difference in composition may introduce differences in chemistry and physical properties.

Steve has tried several methods for generating gas in the simulated waste in his model tank without success. One method that was attempted and worked well the first several attempts is to use the reaction of Al metal with OH^- to generate H_2 . Steve first tried this method with a small plastic bottle and machined Al plate (pages K.14 and K.15). When heated in the water bath, Steve noticed that the swelling slurry collapsed when the temperature reached about 54°C (page K.16). This was repeatable most of the time in the small vessel. While this method worked well with this small system, use of the method in the larger tank nearly resulted in disaster. As the reaction proceeded in the larger tank, the Al plate was heated by the chemical heat of reaction. The higher temperature increased the reaction rate. Too much H_2 was generated and the waste began to uncontrollably swell in the tank. The reaction had to be quenched rapidly. The results of these preliminary experiments are summarized on pages K.17 and K.18. Future work to be carried out in the 18-in. tank is listed on page K.19.

Steve addressed some of the concerns that have been voiced on the use of ultrasound (page K.20). As with most mitigation techniques in which work is performed on the waste in the tank, the use of ultrasound can heat the waste. However, it is believed that the ultrasound would be used intermittently and the total power needed should be about 10% of the radiolytic heat load currently in the tank. The use of ultrasound could enhance corrosion of the waveguide that would be used to deliver the ultrasound to the nonconvecting layer. The most serious concern voiced to date is the issue of sonochemistry. It is known that ultrasound can enhance reactions that would normally not need to be considered. The main effect is cavitation that can raise the temperature in a very localized area to over 1000°C. Therefore, every effort will be made to avoid the possibility of cavitation in the system.

Some of the concerns over the use of ultrasound may also be looked upon as helpful (page K.21). Heating, for instance, is being considered as one of the mitigation techniques. The use of high ultrasound energies that lead to cavitation might also be useful in destroying the organics. For all of these concerns and benefits, extensive experimentation will be needed (page K.22).

Russian work had been cited as evidence that ultrasound might be inappropriate for use in the waste stored in Tank 101-SY. Steve addressed the issues raised in this article (page K.23).

Steve also addressed some of the safety issues associated with using AI in these experiments (pages K.24 and K.25).

Physical Modeling of Tank 101-SY Phenomena with Chemical Simulants

At PNL, chemical simulants are being used by R. T. (Rudy) Allemann to determine how the gases are retained in the waste (page L.2). As in Steve Agnew's experiments, Rudy has also been trying to introduce gases into a simulated waste slurry. Rudy has been concentrating on the conditions necessary to make a simulated slurry with the properties that fit those predicted from the behavior of the waste in Tank 101-SY. He has been using small, 10 cm, plastic jars to do this scouting work. The size of the container will be increased when the proper conditions have been determined (page L.3).

Rudy has tried several methods for generating gas in his slurries (page L.4). He also has tried the AI reaction and has given up on the method. Spargers are currently being investigated.

Rudy has found that the waste slurry must be properly conditioned to achieve cohesive strength (pages L.5 through L.7). Gases are generated only very slowly, but the effects of the intrinsic gas generation can be seen in floating solids and crust formation. Using this technique, Rudy is able to produce a sludge that traps gas and has a yield strength that decreases when heated to a moderate temperature (pages L.8 and L.9). The changes in crystal morphology occur on heating and cooling.

The data described above will be used as input to the numerical model that will be used to describe the slurry layer (pages L.10 and L.11). This model of the slurry layer is different from the one Tom Burke discussed, although both incorporate the yield strength of the material, and was discussed at the July meeting in Atlanta. The data obtained from these tests will be useful in designing a physical model which will be used to verify the numerical model and test remediation and mitigation techniques.

Some of the data that need to be obtained include the variation of the crystal morphology with increasing temperature, changes in physical properties with increasing temperature, and testing of mitigation techniques (page L.12).

In the discussion that followed, it was agreed that it will be important to investigate the nature of the crystals in the nonconvecting layer rather than working on the nature of the bubbles in that layer. Bubbles might coalesce but not be released because the matrix is not broken up. One of the problems encountered by Rudy is that the act of measuring the strength of the simulated nonconvecting layer changes the strength.

Results from Ferrocyanide Studies at Pacific Northwest Laboratory

It was anticipated that more material on ferrocyanide studies would be presented. Additional work is taking place at PNL and at WHC, but no one was available to describe parts of the work. The portion of the work described here was presented by L. L. (Lee) Burger. No copies of Lee's viewgraphs were available.

Since the last meeting in Atlanta, work at PNL has centered on characterization of the laboratory and vendor-produced ferrocyanides. Both the in-plant and the in-farm processes were simulated to yield simulated ferrocyanide waste material. Actual in-plant material was precipitated in the plant where metal recovery was taking place; in-farm material was precipitated in a tank in the tank farm using waste that had already been made alkaline. Because of the differences in the way the ferrocyanide was precipitated, the in-plant material has much more iron, while the in-farm material is expected to be much more pure ferrocyanide. The in-plant material contained about 0.8 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ and 95 wt% NaNO_3 , Na_2SO_4 , and Na_3PO_4 , whereas the in-farm material contained about 25 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ and 54 wt% NaNO_3 and NaNO_2 . The remainder of the mass balance appears to be water. Four other flow sheet variations were investigated. These contained elements such as Cr to simulate the corrosion products and Cl to simulate the contaminant in NaOH. Strontium was added to some of the in-plant scavenging campaigns to precipitate Sr_3PO_4 , thereby lowering the ^{90}Sr in the effluent; Ca_3PO_4 was later used to scavenge the ^{90}Sr because Ca was cheaper than Sr.

Using the thermogravimetric analyses (TGA), Lee and his coworkers have determined that $\text{NaNiFe}(\text{CN})_6$ and $\text{Ni}_2\text{Fe}(\text{CN})_6$ contain about 4 molecules of water. All of these compounds appear to be nonstoichiometric. The material that is freshly precipitated undergoes an explosive reaction in the time-to-explosion test. Apparently, there is sufficient nitrate in this material that the exothermic reaction can occur. Even the material that has been washed two times with demineralized water or demineralized water with a trace of electrolyte explodes in the time-to-explosion tests. All of these materials exhibit complex thermal decomposition and oxidation as evidenced in the differential scanning calorimeter scans. Consistent with the material undergoing rapid decomposition are the results from the TGA in which large mass losses are observed in the range of 240°C to 350°C.

From the DSC results, it appears that the salt mixture, e.g. $\text{NaNO}_2/\text{NaNO}_3$, needs to melt before the exothermic reaction involving the ferrocyanide begins. To test this, Lee used the lower melting eutectic salt mixture $\text{KNO}_3/\text{NaNO}_2$. This eutectic mixture mixed with ferrocyanide yielded a higher decomposition (oxidation) temperature. This was unexpected. Lee has also used AgNO_3 with ferrocyanide and found lower decomposition temperatures, as expected. Thus, the decomposition temperature appears to depend on the nitrate salt. Reactions appear to occur in the molten salt that is produced as the mixture is heated, but there are some open questions on this issue.

Results obtained from the DSC and TGA when using $\text{Ni}_2\text{Fe}(\text{CN})_6$ are different from results with the sodium salts. The use of $\text{KNO}_3/\text{NaNO}_2$ instead of $\text{NaNO}_3/\text{NaNO}_2$ yields a higher reaction temperature as observed with $\text{Na}_2\text{NiFe}(\text{CN})_6$.

The actual in-plant material stood a good chance of being oxidized to ferricyanide [$\text{NaNiFe}(\text{CN})_6$], so this material was also tested. Results indicate that the critical temperature is lower for $\text{NaNiFe}(\text{CN})_6$ than for the $\text{Na}_2\text{NiFe}(\text{CN})_6$. Both the as-prepared and the washed simulated in-plant materials gave the same time-to-explosion curves.

During a portion of the in-farm campaign, it was noted that the ^{60}Co was high in the effluent that was ready to be sent to the trench. To lower the ^{60}Co content of the effluent, NaS was added along with Ni_2SO_4 to precipitate NiS that scavenged the ^{60}Co as CoS. To observe the effect on the thermal behavior of simulated $\text{Na}_2\text{NiFe}(\text{CN})_6$, 5 wt% CoS was added to the mixture of $\text{Na}_2\text{NiFe}(\text{CN})_6$, NaNO_3 , and NaNO_2 . This mixture had an exotherm in the DSC that was about 10°C lower than without CoS. Nickel sulfide and CoS have nearly identical properties. Other contaminants such as Ni, Cr, and Fe hydroxides had little effect on the temperature at which the exotherm occurred.

Analytical methods of determining the presence of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and related compounds have not yet been developed, but work has begun. One possible, but not unequivocal, method to determine the presence of $\text{Na}_2\text{NiFe}(\text{CN})_6$ is to determine if there is any water insoluble ^{137}Cs in the waste. Although there are other possibilities for why ^{137}Cs would be insoluble in water, one might use this criteria as a quick indicator for the presence of significant $\text{Na}_2\text{NiFe}(\text{CN})_6$.

One of the observations at Oak Ridge National Laboratory is that $\text{Na}_2\text{NiFe}(\text{CN})_6$ is soluble or hydrolyzes in strong base. Some scouting experiments were carried out with $\text{Na}_2\text{NiFe}(\text{CN})_6$ in 0.1 M and 1 M NaOH. In 1 M NaOH, about 125 ppm NH_3 gas was detected and in 0.1 M NaOH 25 ppm NH_3 was observed. The hydrolysis of CN^- yields NH_3 as one of the products. It was uncertain how much of the $\text{Na}_2\text{NiFe}(\text{CN})_6$ in these experiments was decomposed.

Discussion of the H_2 Mitigation/Remediation Report

Before the meeting, J. L. (John) Deichman, Manager Tank Waste Safety Project, WHC, had requested that the Science Panel members review and comment on the document entitled Mitigation/Remediation Concepts for Hanford Hydrogen Gas Generating Waste Tanks. No written comments were received, but several general comments were made at the meeting. The discussion of these comments is summarized below.

The Science Panel members felt that the tone of the document gave the feeling that the document was written in response to a threat rather than from a scientific need to develop mitigation and remediation concepts for Tank 101-SY and other tanks in which H_2 is being generated. Thus, it should be stated up front that there are scientific and engineering studies that need to be performed to develop remediation and mitigation concepts. These studies need to be performed first, before any decision is made on which technique is the best. All priority issues should be studied fully. All stakeholders, those with an interest in the safe disposition of the safety issues in these tanks, should be consulted. To bring this tone to the document, there needs to be more statements up front about the limitations of this document, in particular, and what studies are needed to provide a credible resolution to the safety issues.

It was revealed that there appears to be a push to have ultrasound in the tank by June 1992. This statement seemed to be reflected in the tone of the document. The Science Panel members cautioned that taking a shortcut to the normal scientific and engineering approach to a potentially difficult problem might lead to, at best, some process that did not work or, at worst, to an exacerbated safety problem. This reaction by the Science Panel members, including the candidates for the Science Panel, was quite strong. The Science Panel members reminded those present of the statement, made over a year ago, not to do anything to the waste in the tank until the chemical and physical mechanisms were clearly understood and the implications of any actions could be predicted. It is clear that understanding has not yet been achieved.

The Science Panel members discussed how the concepts had been ranked at WHC. In general, the Science Panel members disagreed with some of the details of the ranking. For instance, they thought that some of the more simple options should have ranked higher. It was pointed out that for some, such as N_2 sparging, while the concept seems simple, engineering the process in a 23-m-diameter tank with about 10 m of waste to get distribution of the gas is not simple. The Science Panel members felt that the "zero option" should have been treated more completely and ranked along with the other options. With respect to the overall ranking process, it was observed that the concepts ranked quite close to one another. The top ten concepts had ranking scores that were within about 10% of each other. This would suggest that the ranking scheme should be reviewed. The ranking of these concepts at this stage would seem to be premature.

There was a discussion on the normal approach to scaling these techniques from the laboratory to the actual plant. It was not obvious to the Science Panel members that a series of scaled tests were to be performed. It seemed that to make the pilot-scale test the actual implementation in the tank would be a mistake. The Science Panel members encouraged the use of several scaled experiments designed to test not just one technique, but several. A lot could be gleaned from a 400 L test. In the end, the Science Panel members suggested a less ambitious schedule to remediation or mitigation than was portrayed in the document.

A task force for each set of options is needed. Although the working groups that were responsible for each section of this document included one or two people from offsite, the available expertise was insufficient to do a credible job of evaluating each option, determining the studies that are needed to ensure that the method will work, and deciding what will be needed to scale up the process. Task forces need to be pulled together. If the pressure to have something in the tank by June 1992 is removed, then the task forces could be used to accomplish the needed ranking and define the needed studies within six months.

The Science Panel members wanted to know if they would be receiving a revised document to see if the comments and suggestions that they had made would be incorporated. The staff member from WHC that was present at the meeting indicated that the changes and comments would be incorporated and that the Science Panel members would receive copies of the updated documents.

Discussion of the Ferrocyanide Mitigation/Remediation Report

The Science Panel members had also been requested to review the report entitled Mitigation/Remediation Concepts for Ferrocyanide Waste Tanks. Many of the same general comments made on the report entitled Mitigation/Remediation Concepts for Hanford Hydrogen Gas Generating Waste Tanks applied to the ferrocyanide report.

One specific comment was noted. In Section 4.3.1 there is a set of three criteria to determine whether ferrocyanide waste is dangerous. In Section 5.3.2, only one of these criteria is needed. The WHC representative indicated that there was a mistake in the wording and these words would be changed to make sure the two sections agree.

It was not clear to the Science Panel members that all of the techniques for remediation or mitigation had been identified. If a new method was identified, how would this method be evaluated? Would it be evaluated? This was seen as another indication that the system was pushing decisions too fast without enough evaluation.

Working Group Coordination Meeting - Hydrogen

Two video tapes of the activity in Tank 101-SY were shown. It was clear from the tapes that the "crust" was not the solid material that had been envisioned by the Science Panel members. Parts of the crust material were definitely hard and other parts appeared to be like oatmeal. These tapes served as introductory material to G. D. (Jerry) Johnson's presentation.

Crust samples have been collected from the tank in two "windows" (periods of time during which work may be performed in the tank by people outside the tank). Crust samples were collected to address one major safety concern: Does the crust contain sufficient organics and insufficient moisture that the crust could burn or be caused to ignite while a core sample is being taken? The data for the crust samples obtained during Windows A and C are shown on page M.1. For the crust material to be flammable, there would have to be about 3 wt% organics and less than 20% moisture. Total exotherms would have to exceed 90 cal/g to create a safety concern.

Preliminary results from the Window C (May 1991 core samples, comprising 22 segments) are summarized on the next three pages (pages M.2 through M.4). It took about 7 days to obtain these samples. Just before the window closed, about 7 to 10 days later, three more segments were obtained from the bottom of the tank. These were taken to determine if there was any significant settling during that time. The segments are 0.48 m (19 in.) in length and are numbered from the top of the waste. The number of segments is calculated based on the distance from the top of the riser to the bottom of the tank and to the top of the waste. The last segment should be full; the first segment should be partially filled. Segments 4 through 14 were observed to be identical, consisting of slush-like material. Segments 14 through 22 were identical in appearance, consisting of clay-like material. Nitrate and nitrite appear to be uniformly distributed from top to bottom of the tank (page M.2). There are two NO_3 and one NO_2 data points that lie to the right of the others in the figure on page M.2. These appear to be due to analytical error. Moisture levels in the tank appear to be greater in the convecting zone than in the nonconvecting zone (page M.3). Organic carbon levels are significantly higher in the nonconvecting layer than in the convecting layer (page M.3). The preliminary results are tabulated on page M.4. The high level of Cr has also been noted in Tank 103-SY. This high level of Cr is surprising, but the fact that it is in the bottom layer is not. As noted at the bottom of the table, results from more analyses are pending. Another surprise was the results from the CN analyses. Although these results are not reported in the table on page M.4, the values have been in the 300 ppm to 400 ppm range.

The issue of a crust burn appears to be nearly resolved (page M.5). There appears to have been sufficient samples collected to support the rejection of the crust burn concept. However, are there any additional samples or data needed to close this issue? The crust composition from the analyses and the measured energies from the H_2 -burn studies at the U.S. Bureau of Mines will be used in the next safety study.

Gases are being monitored in Tank 101-SY using several different methods and at different times (page M.6). Recent analyses of the grab samples indicate that the steady-state H_2 concentration is about 11 ppm at a flow rate in the tank of $0.28 \text{ m}^3/\text{s}$ (600 cfm). One of the gases that needs to be analyzed for its steady-state value is N_2O .

Mitigation and remediation was discussed briefly (page M.7). Mitigation means that the episodic release of gases from the tank are removed such that the gas release is more even or continuous. This yields gas concentrations that are below the lower flammability limit for H_2 . In a remediation technique, the goal is to reduce gas generation to zero or near zero. Several methods under each topic have been conceptualized.

Several questions were raised concerning the need for analyses on the waste material (page M.8). Is there a need for the organic analyses? There appears to be a need based on the need to support the choice of a mitigation or remediation option. Are there sufficient facilities to perform the analyses that result from the sampling program? For instance, on a single core consisting of 22 segments, over 3000 analyses will be performed. Based on what we know today, is the mixture of HEDTA/EDTA the correct mixture to be using in the simulated waste studies?

Input from the Science Panel is needed in a more timely manner (page M.9). In part, the minutes for the meetings need to be published much more rapidly, but feedback on the state of the mechanisms needs to be made more frequently. There needs to be more interaction on the part of the Science Panel with the participants in the scientific work and more indication as to what parts of the experimental program are worth pursuing and which ones ought to be redirected.

Working Group Coordination Meeting - Ferrocyanide

A presentation by R. J. (Bob) Cash was made on the general direction of the Ferrocyanide Stabilization Program (page N.1). Bob started by relating the results of a recent analysis of the gases in Tank 104-BY. The results indicate that the vapor space in this passively vented tank^(a) has 0.12% H_2 and between 25 ppm (by cryotrap) and 200 ppm (by gas chromatography) NH_3 . These are very preliminary results; more data need to be collected and better data analysis is needed.

Under the current direction of the ferrocyanide program (page N.2), in situ safe storage will be the method of choice unless there is some compelling reason to remove the waste prior to retrieval and final disposition of the waste. This approach is based on the currently available data that suggest the material in most of the tanks will not react. There are three factors used in this analysis: the temperature of the waste is cool and cooling, the moisture content is greater than 20%, and the concentration of ferrocyanide at any given point in the tank is insufficient to cause a runaway reaction.

To ensure that the waste remains in a safe condition, the temperature will need to be monitored to ensure that the temperature is below the value known to cause an unsafe condition (page N.3). As has been discussed in the past both at WHC and in past Science Panel meetings, a method has not been found to monitor the waste temperature to ensure that no hot spot exists in the waste. Evaluation of infrared

(a) A passively vented tank is one that has been physically removed from contact with sources of water and the only ventilation is that which is caused by changes in atmospheric pressure through a high efficiency particle filter.

techniques indicates that this methodology does not have sufficient sensitivity to allow detection of the smallest concentrated mass considered to represent a problem. In situ moisture measurement techniques are also needed for much the same reason that the temperature sensor is needed.

The possibility of the waste concentrating into a small enough volume to be a problem is also difficult to prove or disprove (page N.4). Three flow sheets were used, two of which can be classified as in-plant processes. The first in-plant material represents about 70% of the ferrocyanide produced at the Hanford site. It contains about 65% water. The remaining in-plant material, about 10% of the total ferrocyanide, was produced at T Plant on the Hanford site. The in-farm material represented about 20% of the total ferrocyanide. It was precipitated from a solution containing 0.0075 M $\text{Na}_2\text{NiFe}(\text{CN})_6$. The ferrocyanide materials were flocculent and difficult to settle. After being allowed to settle for several days, the supernatant liquids were pumped to a crib. It is thought that the precipitates were laid down in uniform layers and that hot spot areas did not get a chance to build. The bottoms of some tanks are sloped so that at the center the ferrocyanide layer might be a little thicker than at the edges of the tank. Because of the geometry of the layers in the tanks, it is felt that some tanks may require only two core samples to characterize the entire tank contents, whereas other tanks will require more cores, especially those with hard layers in them. Plans have been made to sample three tanks during fiscal year 1992. There is a concern, however, that there may not be enough funds to accomplish this task.

The Science Panel members requested a graphic that shows the various processes, process names, volumes, and relative amounts. This would serve to relieve some of the confusion surrounding the ferrocyanide processes.

Assistance from the Science Panel members was solicited concerning the areas shown on page N.5. The logic diagram for the program should also be reviewed (pages N.6 and N.7).

Executive Session

During the Executive Session, it was decided that several letters should be written covering different topics depending on the addressee. Copies of these letters are shown on pages O.1 through O.18. Included in these letters is the letter written by the Executive Secretary to J. L. Deichman in which the meeting was briefly summarized (page O.1).

References

- Babad, H., J. L. Deichman, B. M. Johnson, D. K. Lemon, and D. M. Strachan. 1991. Mitigation/Remediation Concepts for Hanford Hydrogen Gas Generating Waste Tanks, WHC-EP-0516 (PNL-7875), Westinghouse Hanford Company, Richland, Washington.
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Appendix A

Meeting Agenda

AGENDA

TANK WASTE SCIENCE PANEL MEETING

NOVEMBER 11-13, 1991
RED LION MOTOR INN
Pasco, Washington

MONDAY, NOVEMBER 11, 1991 - GAS GENERATING TANKS

8:00 AM	Breakfast	
8:30 AM	Opening Remarks	TH Dunning
8:45 AM	Update on Gas Release from Tank 241-SY-101	DA Reynolds
9:15 AM	Report on Chemical Analyses of Core Samples	DL Herting
10:00 AM	Break	
10:15 AM	Results from Laboratory Gas Generation Studies	DL Herting
10:45 AM	Summary of Results from Tests at PNL	SA Bryan
11:30 AM	Summary of Results from Tests at ANL	D Meisel
12:15 N	Lunch	
12:45 PM	Summary of Results from Tests at GIT	EC Ashby
1:45 PM	Recent Analytical Results on Organics	JA Campbell
2:15 PM	Summary of Physical Modeling at WHC	TM Burke
3:00 PM	Summary of Work at LANL	SF Agnew
3:45 PM	Summary of Physical Modeling At PNL	RT Allemann
4:30 PM	Discuss H ₂ Mitigation/Remediation Report	

TANK WASTE SCIENCE PANEL MEETING

TUESDAY, NOVEMBER 12, 1991 - FERROCYANIDE WASTE TANKS

8:00 AM	Breakfast	
8:30 AM	Opening Remarks	TH Dunning
8:45 AM	Results from Ferrocyanide Studies At PNL	RT Hallen/LL Burger/RD Scheele
9:45 AM	Results from Ferrocyanide Studies At WHC	DB Bechtold
10:45 AM	Discussion of Ferrocyanide Work	
11:15 AM	Discussion of Ferrocyanide Mitigation/ Remediation Report	
12:00 N	Lunch	
12:30 PM	Working Group Coordination Meeting - Hydrogen	
1:30 PM	Working Group coordination Meeting - Ferrocyanide	
2:30 PM	Break	
3:00 PM	Executive Session	
5:00 PM	Adjourn	

TANK WASTE SCIENCE PANEL MEETING

WEDNESDAY, NOVEMBER 13, 1991

Washington State University Center
Auditorium, 100 Sprout Road
Richland, WA

8:30 AM	Opening Remarks	WW Schulz
9:00 AM	Results from the Chemical Mechanisms Studies on The Generation of Gas in Tank 241-SY-101: Thermal Mechanisms	EC Ashby
10:00 AM	Results from the Chemical Mechanisms Studies on the Generation of Gas in Tank 241-SY-101: Radiochemical Mechanisms	D Meisel
10:45 AM	Break	
11:00 AM	Physical Mechanisms of Gas Generation and Release in Tank 241-SY-101	RT Allemann/TM Burke/LR Pederson
12:00 N	Adjourn	
1:00 PM	Panel members are requested to attend the Hanford Technology Exchange (Battelle Auditorium)	

Appendix B

List of Attendees

LIST OF ATTENDEES

<u>ATTENDEE</u>	<u>ORGANIZATION</u>
Stephen G. Agnew	Los Alamos National Laboratory
Rudolph T. Allemann	Pacific Northwest Laboratory
Eugene C. Ashby	Georgia Institute of Technology
Harry Babad	Westinghouse Hanford Company
Roger M. Bean	Pacific Northwest Laboratory
Ned E. Bibler	Westinghouse Savannah River Site
Samuel A. Bryan	Pacific Northwest Laboratory
Leland L. Burger	Pacific Northwest Laboratory
Thomas M. Burke	Westinghouse Hanford Company
Robert J. Cash	Westinghouse Hanford Company
David O. Campbell	Oak Ridge National Laboratory
Thomas H. Dunning, Jr.	Pacific Northwest Laboratory
Billi Hudson	
Benjamin M. Johnson, Jr.	Pacific Northwest Laboratory
Gerrald D. Johnson	Westinghouse Hanford Company
Walter G. Klemperer	University of Illinois - Urbana
Dani Meisel	Argonne National Laboratory
Larry R. Pederson	Pacific Northwest Laboratory
Daniel A. Reynolds	Westinghouse Hanford Company
Glenn A. Russell	Iowa State University
Duane D. Siemer	Westinghouse Idaho Nuclear Company
Wallace W. Schulz	Consultant
Denis M. Strachan	Pacific Northwest Laboratory
William J. Thomson	Washington State University
Graham B. Wallis	Dartmouth College

Appendix C

Further Analysis of Tank Level Data

FURTHER ANALYSES OF TANK LEVEL DATA

**KEVIN ANDERSON
DENIS STRACHAN**

PRESENTED TO:

**TANK WASTE SCIENCE PANEL
NOVEMBER 11-13, 1991
RED LION INN
PASCO, WASHINGTON**

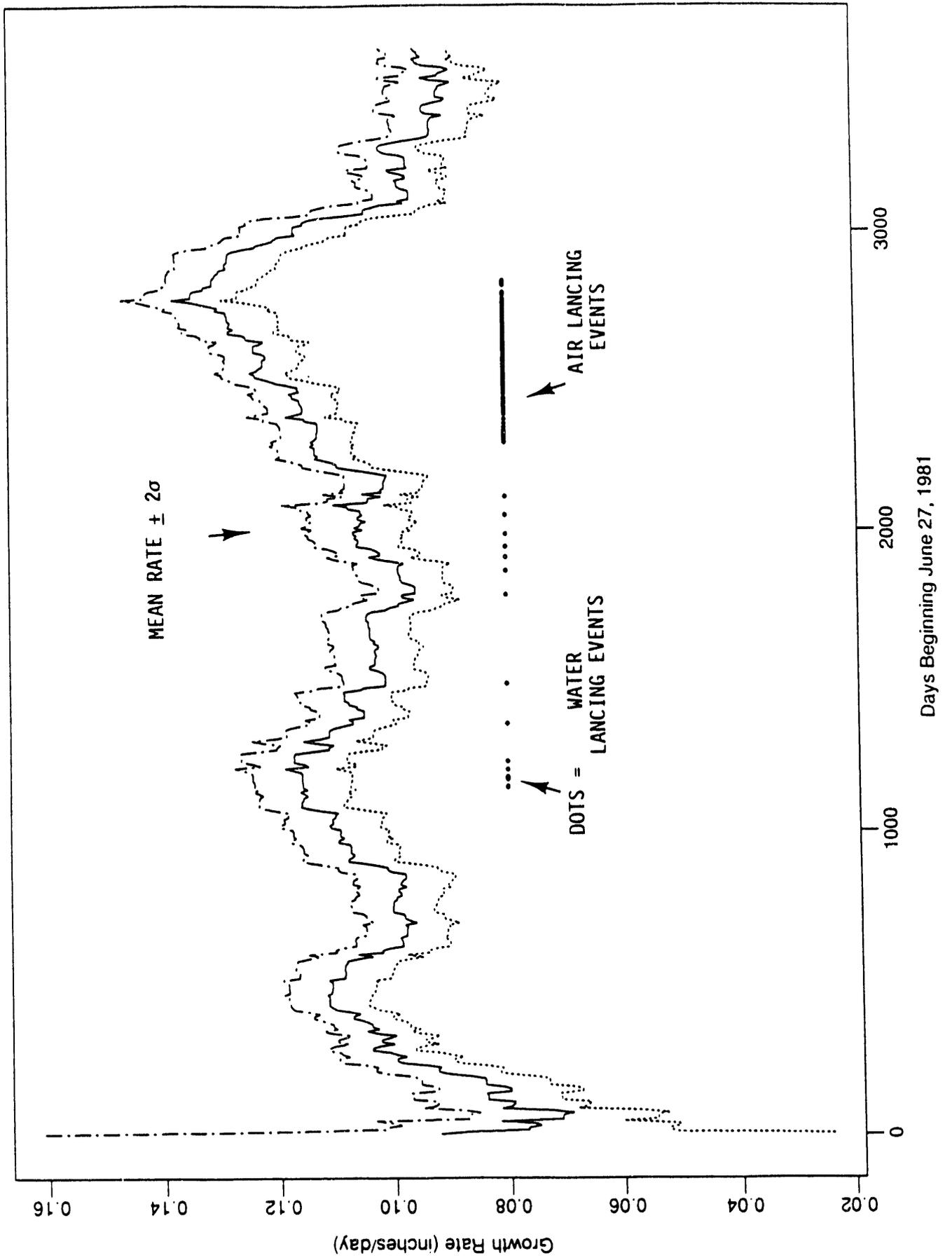
— FURTHER ANALYSES OF TANK LEVEL DATA —

ANALYSIS OF DAILY SLOPE JUNE 1981 TO JUNE 1991

C.2

PACIFIC NORTHWEST LABORATORY

Tank 101-SY Growth Rate Since June 27, 1981



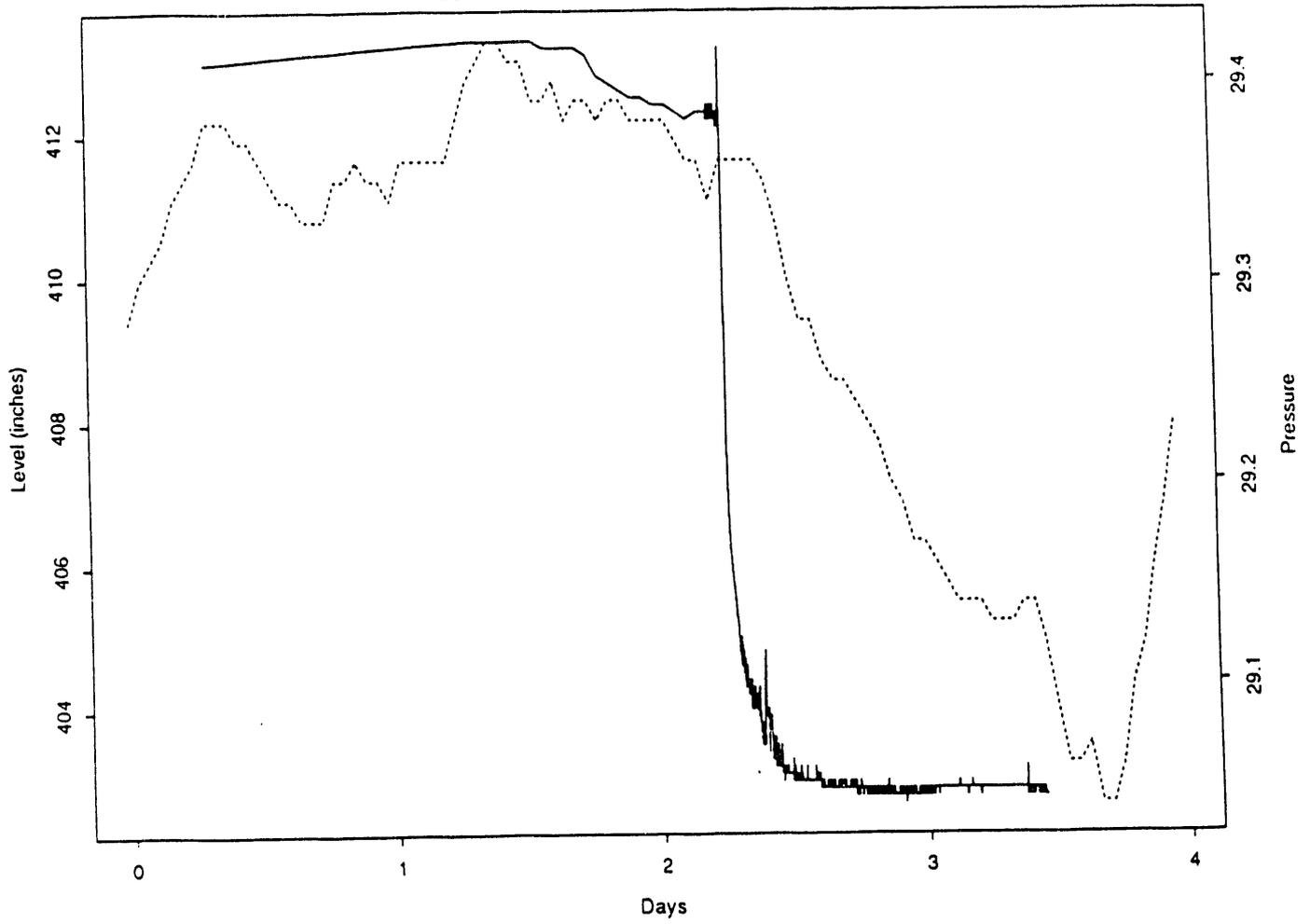
— FURTHER ANALYSES OF TANK LEVEL DATA —

CORRELATION OF GAS RELEASE EVENT WITH ATMOSPHERIC PRESSURE

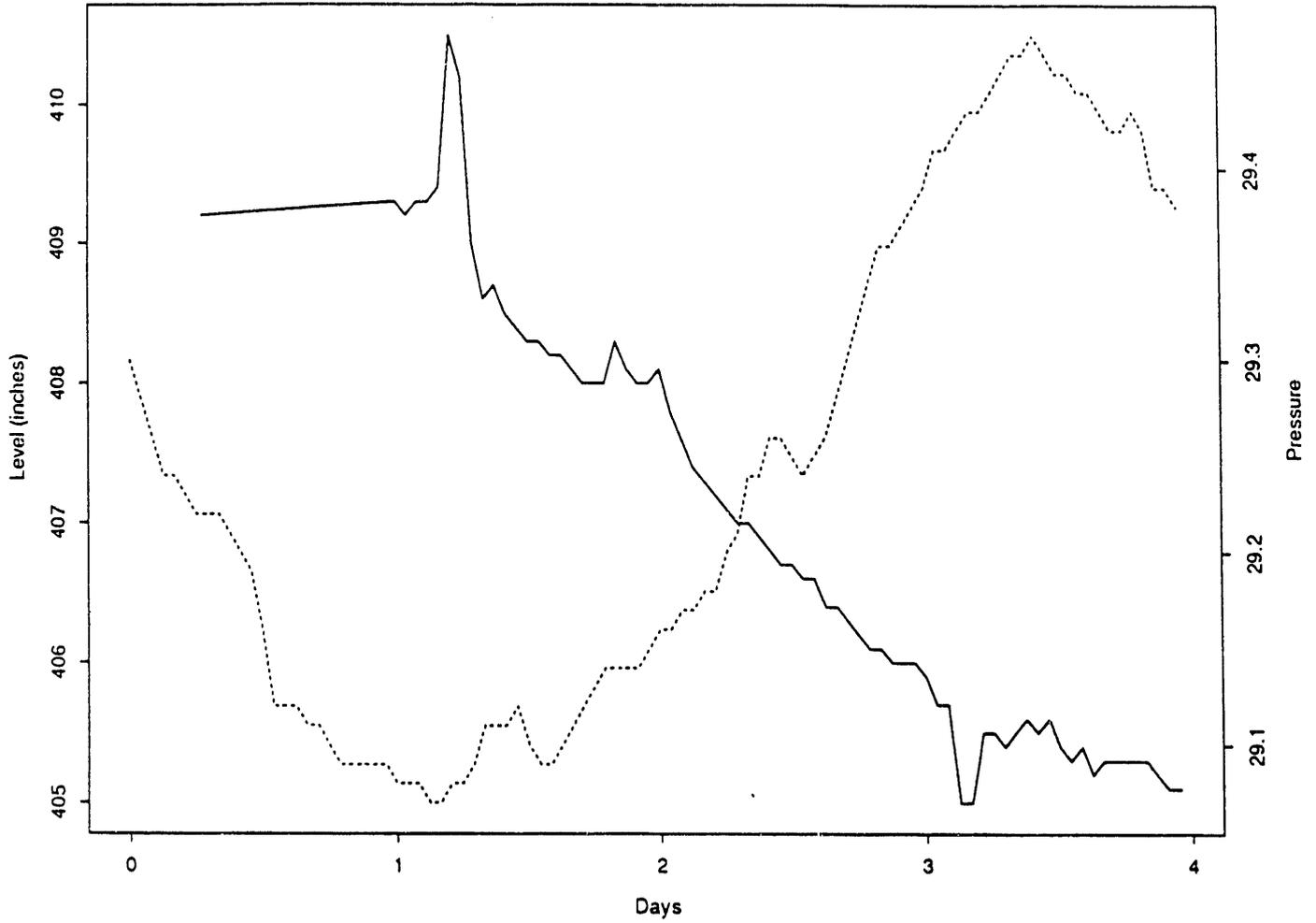
C.4

PACIFIC NORTHWEST LABORATORY

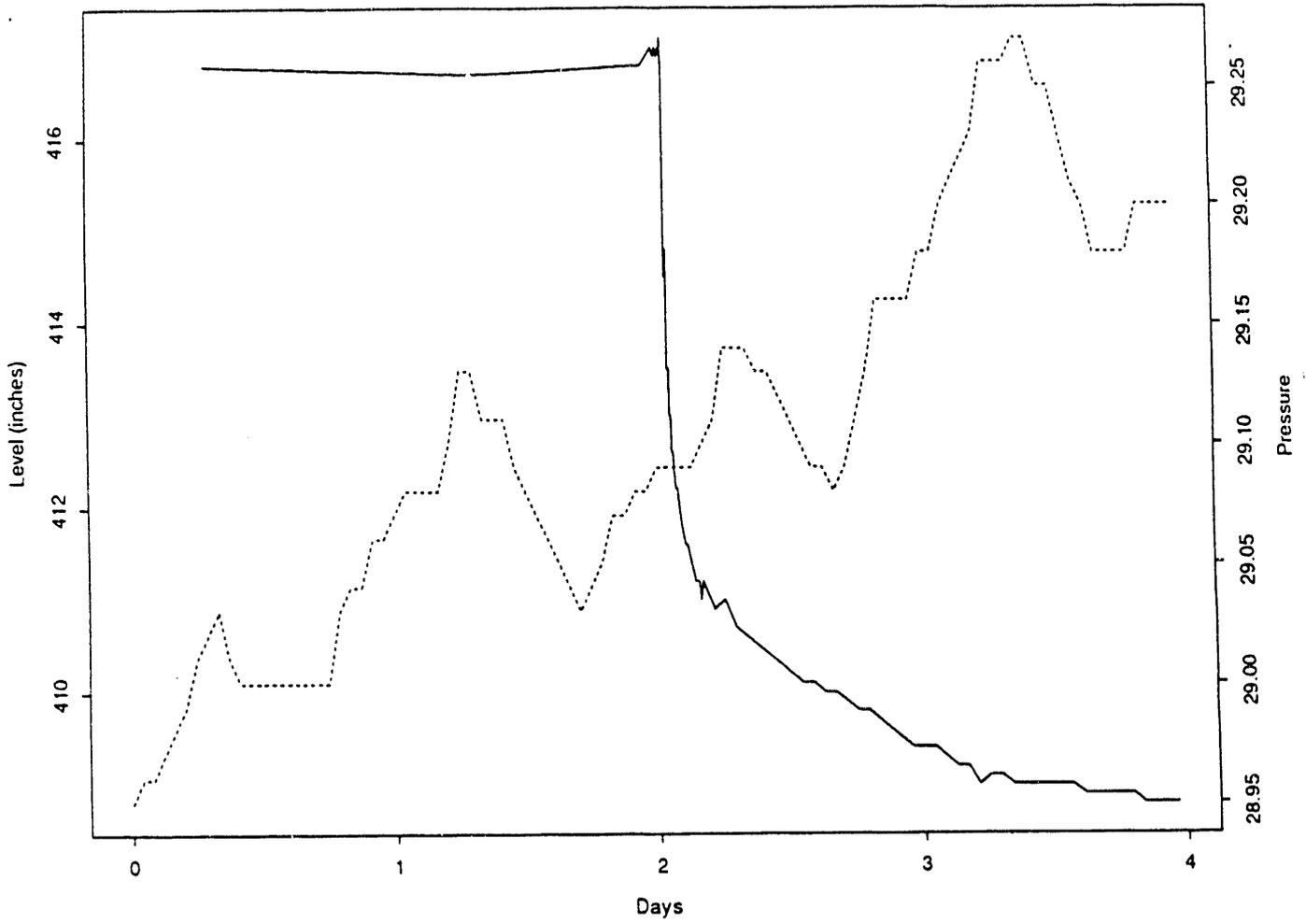
The October 24, 1990 BURP
Level and Barometric Pressure



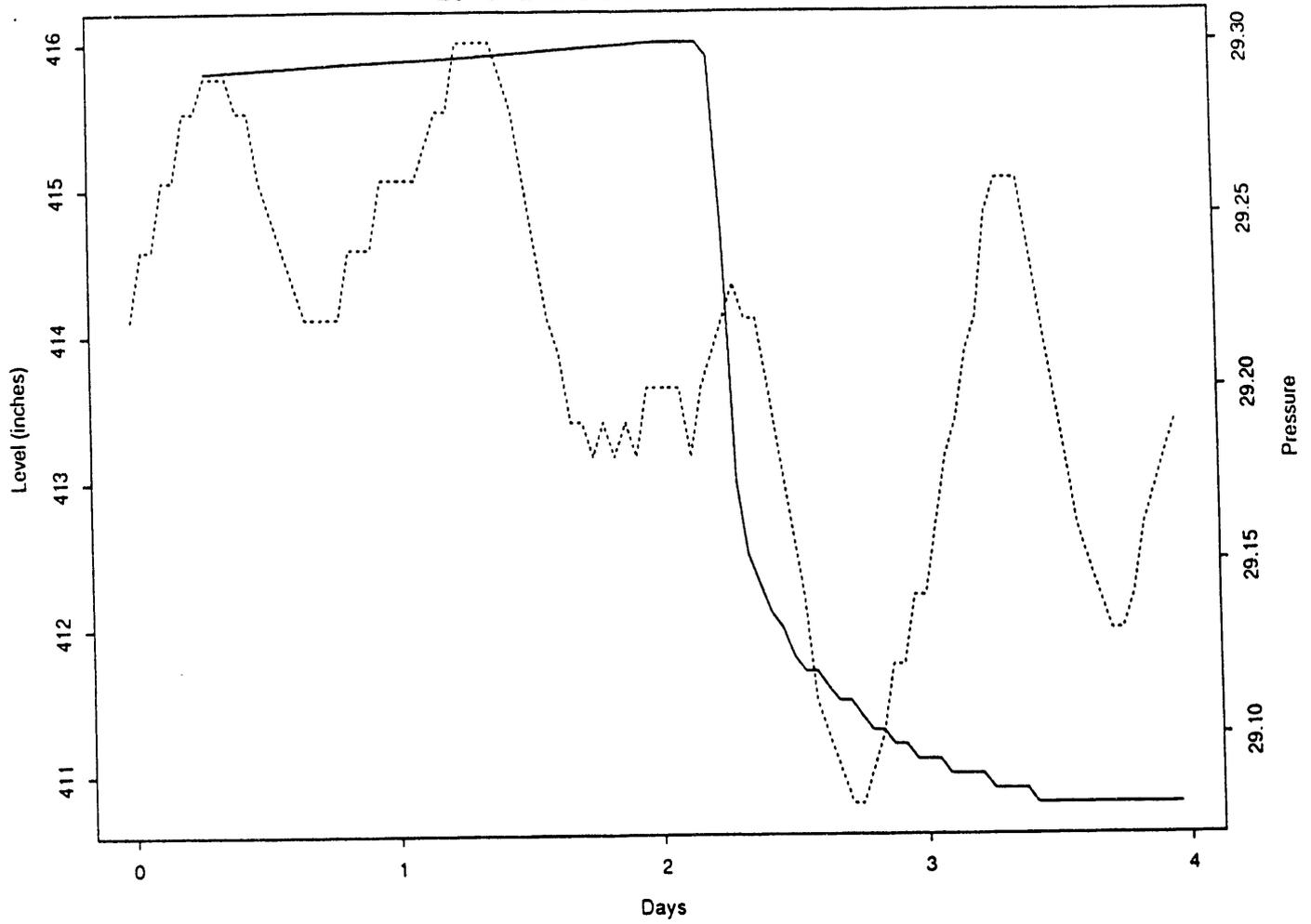
The February 15, 1991 BURP
Level and Barometric Pressure



The April 19, 1990 BURP
Level and Barometric Pressure



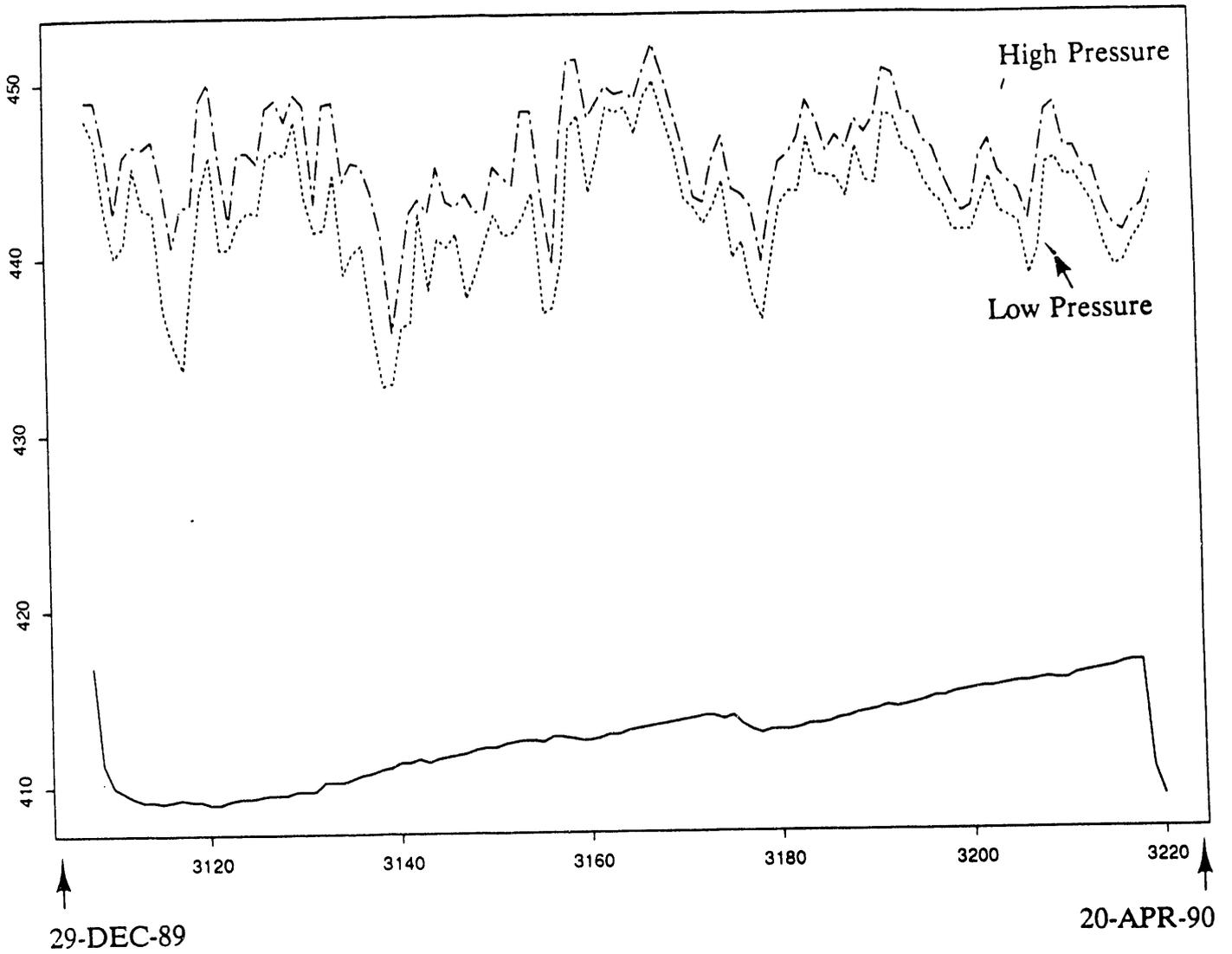
The August 5, 1990 BURP
Level and Barometric Pressure



Low Pressure/High Pressure
Tank Level

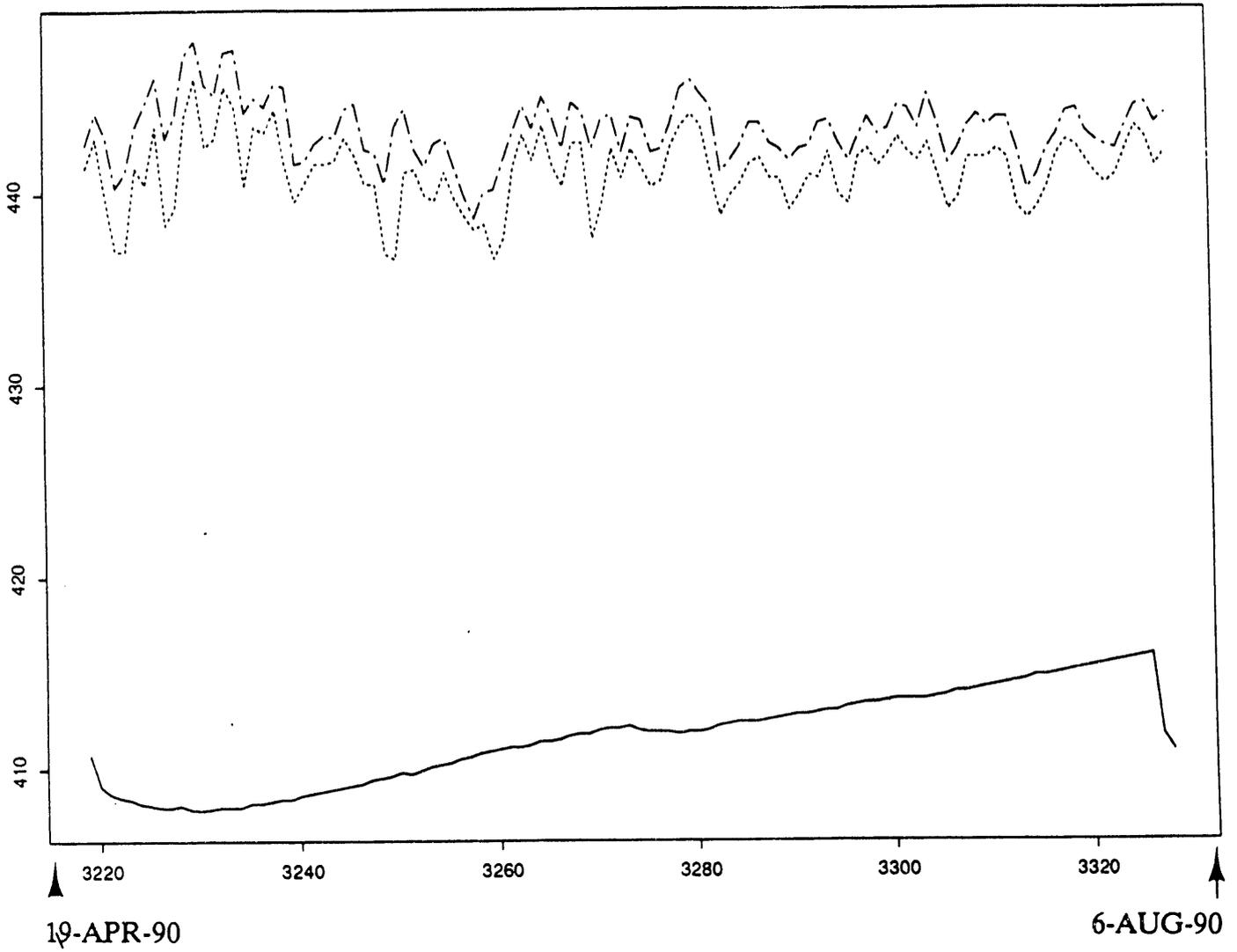
12/29/89 - 4/20/90

Meteorological Data



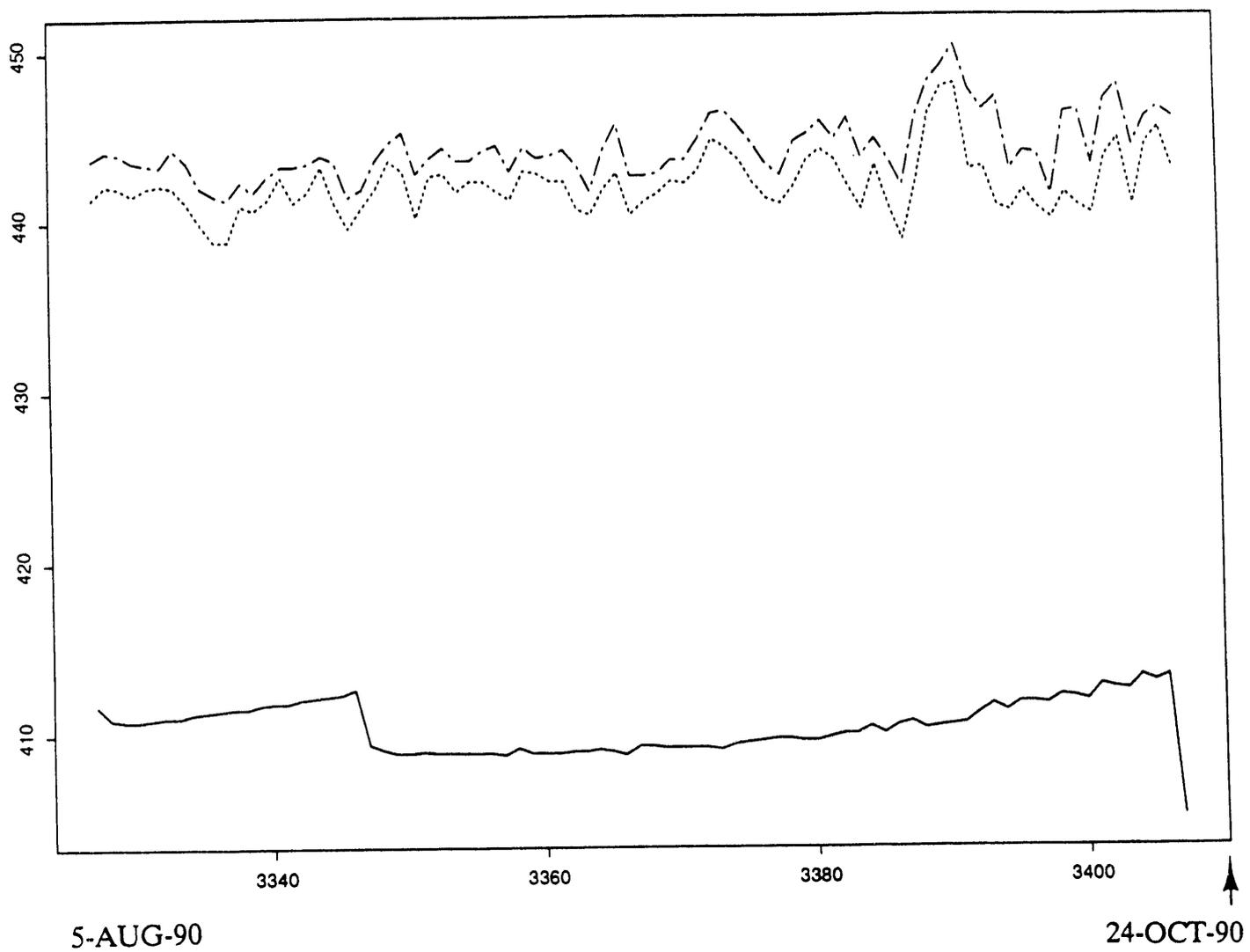
4/19/90 - 8/6/90

Meteorological Data



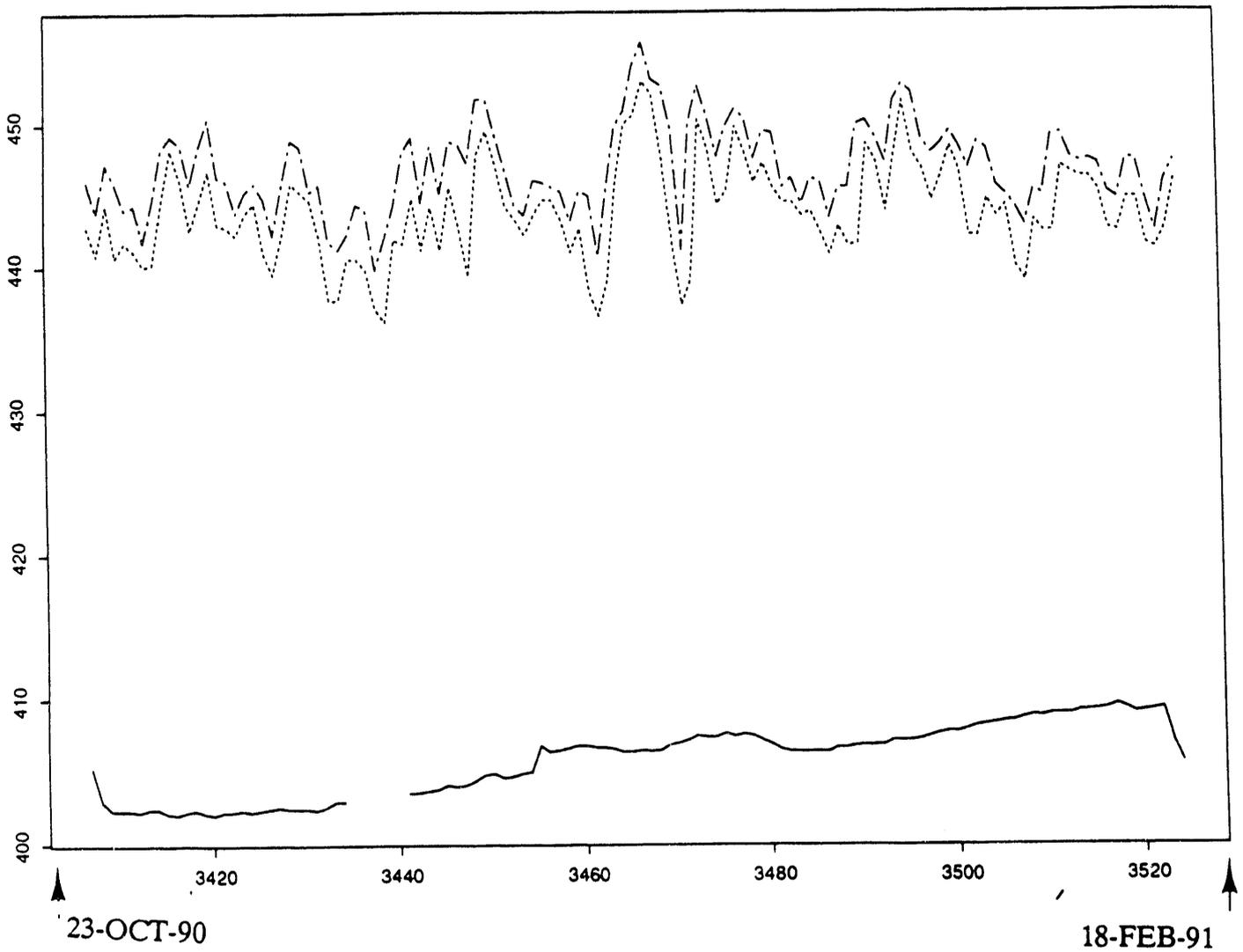
8/5/90 - 10/24/90

Meteorological Data



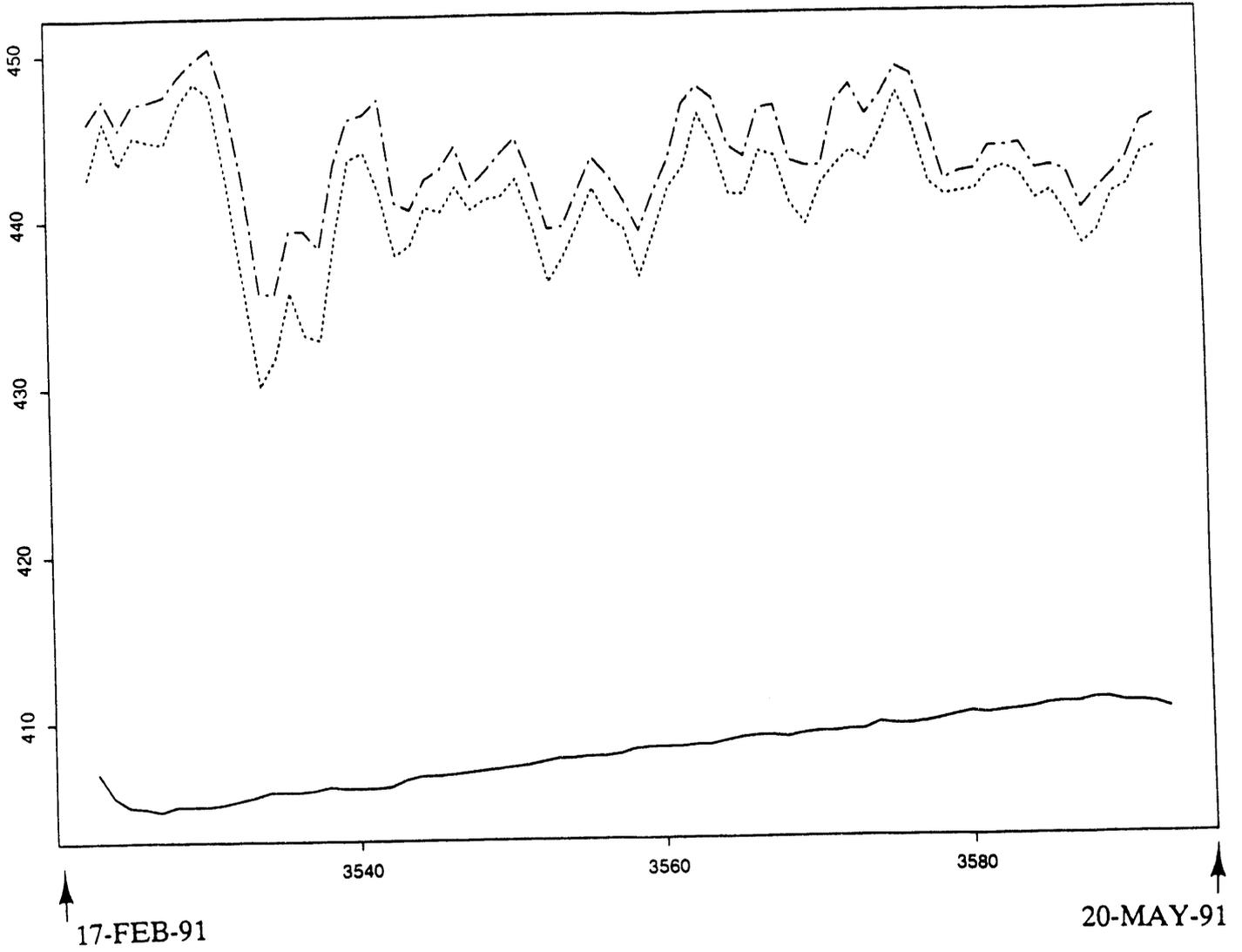
10/23/90 - 2/18/91

Meteorological Data



2/17/91 - 5/20/91

Meteorological Data: Pressure



Appendix D

101-SY Vent Gas Composition

101-SY VENT GAS COMPOSITION

to

Tank Science Panel

by

Daniel A. Reynolds

Westinghouse Hanford Company

November 11, 1991

VENT GAS COMPOSITION

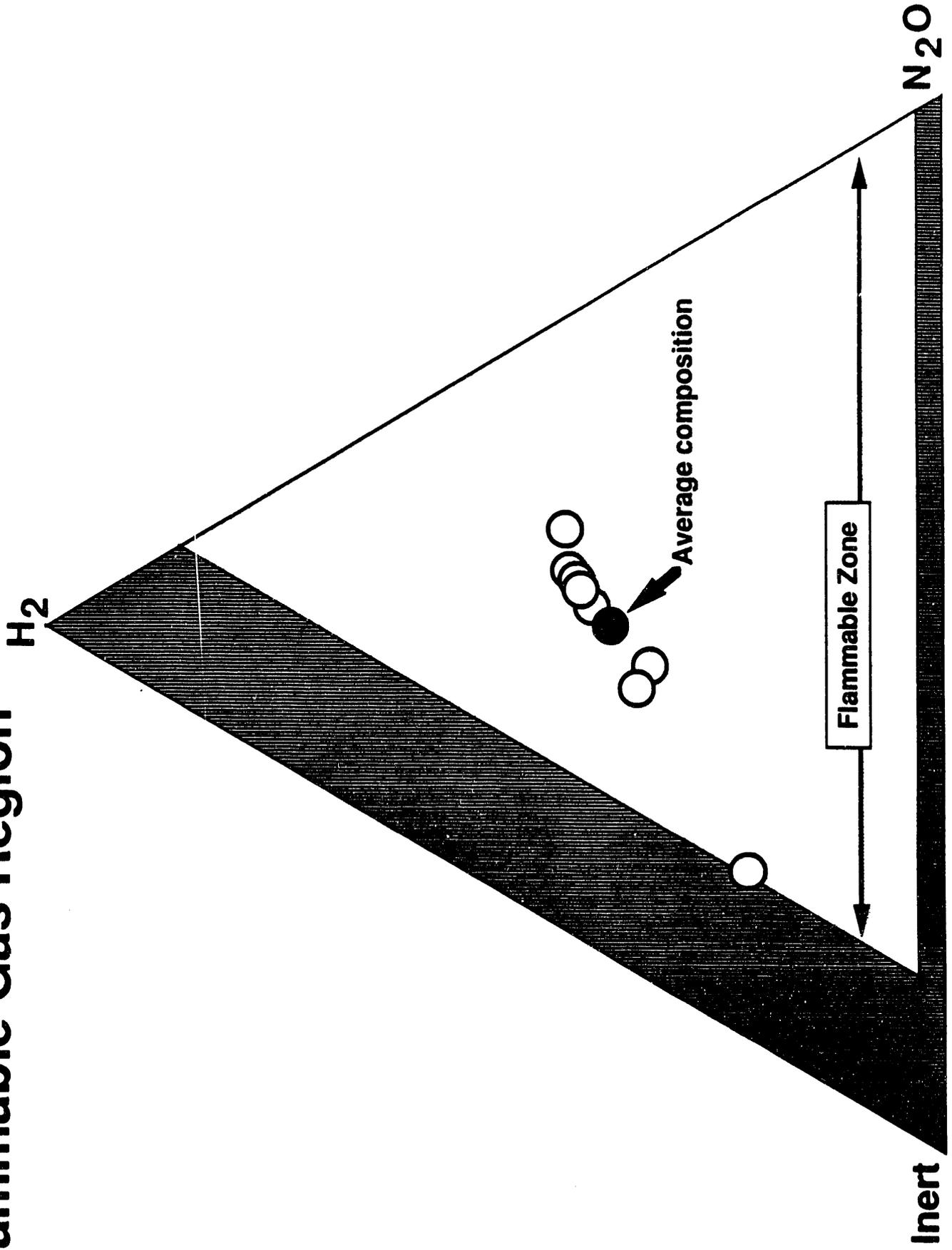
WHY GAS COMPOSITION

- **Safety concerns**
- **Gas generation mechanism**

MEASURED BY MASS SPEC

- **Grab samples from vent**
- **On-line mass spec**

Flammable Gas Region



ESTIMATED GAS COMPOSITION

H₂	39%
N₂O	31%
N₂	29.5%
Other	.5%

**Based on grab samples
Curtesy of R. T. Allemann, PNL**

AMMONIA

- **Present in off gas**
- **OVM Data from Tank Farm Stack**
- **Integrated OVM data to get volume of ammonia**
- **Integrated H₂ data to get volume of vent gas**
- **Estimated percentage of Ammonia**

WATER

- **Water present at saturation**
- **On-line mass spec indicated up to 18% water**
- **Used ProChem to model chemical equilibrium**
- **Gibbs-Duhem equation to get activity of water (0.42)**

BEST ESTIMATE OF GAS COMPOSITION

H₂	36%
N₂O	28.5%
N₂	27%
H₂O	4%
NH₃	4%
Other	.5%

ON-LINE MASS SPEC

- **Gives different results**
- **Nitrous oxide must be calculated off-line**
- **On going problem solving**

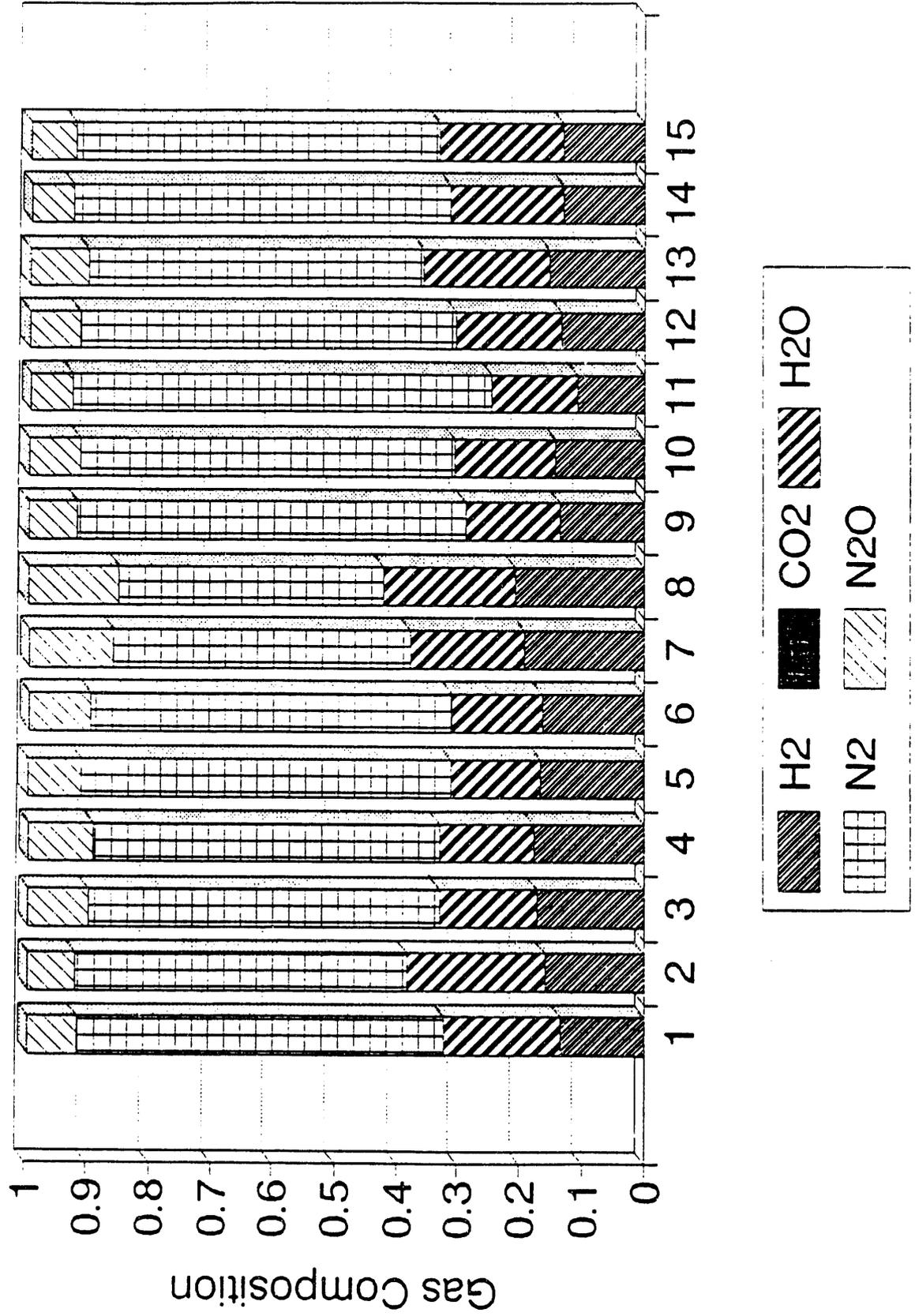
ON-LINE MASS SPEC COMPOSITION ESTIMATE

H₂ 21%

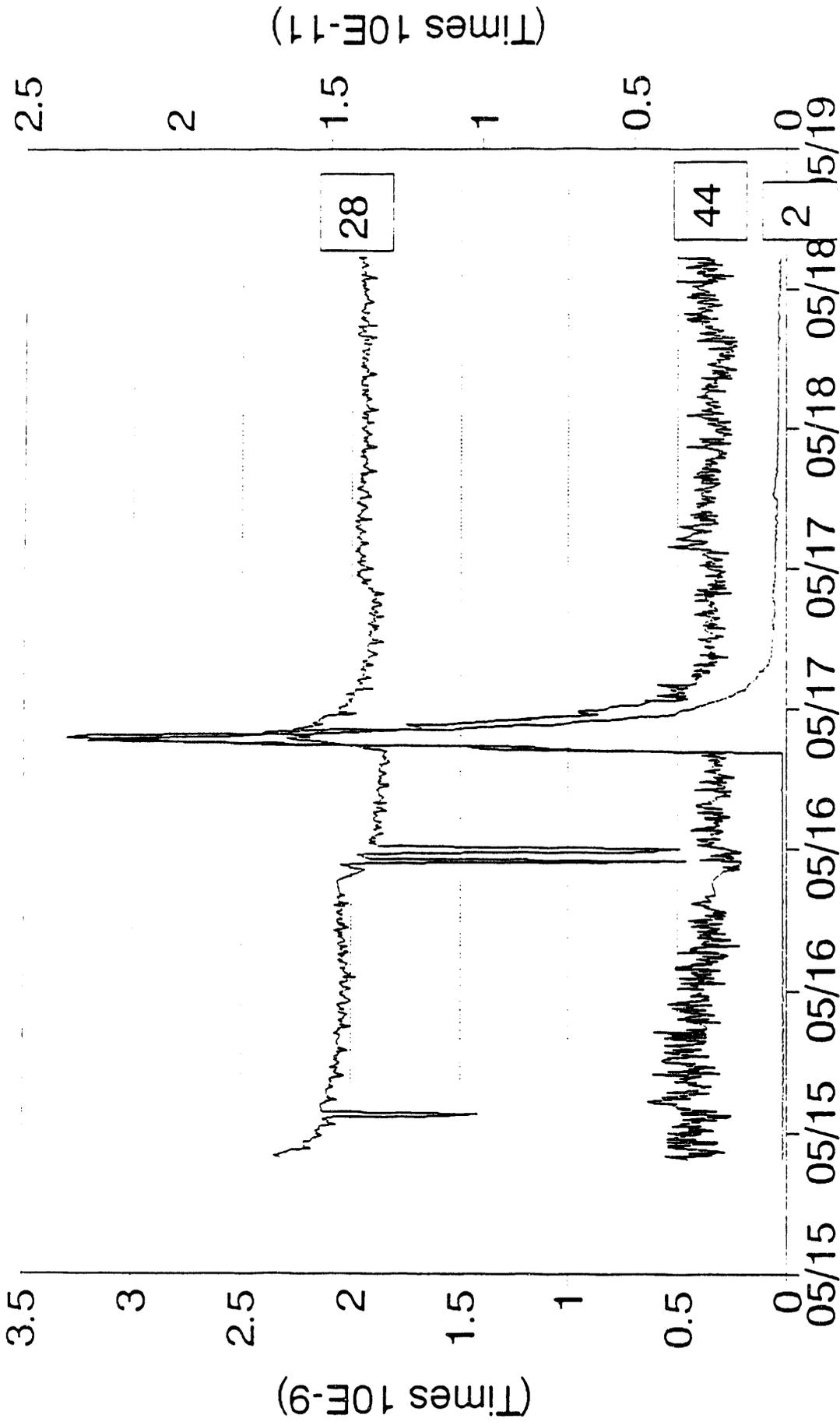
N₂O 16%

N₂ 63%

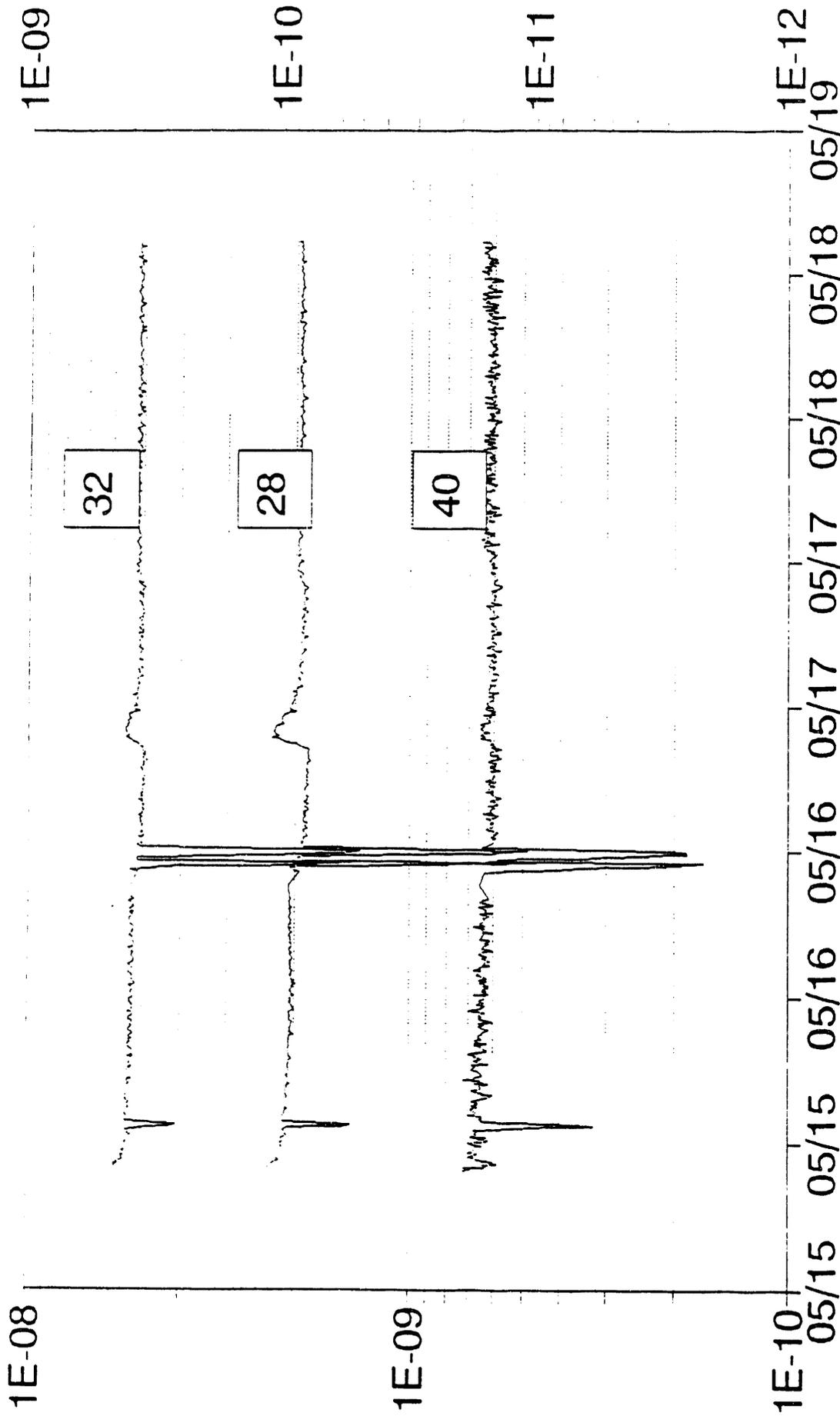
101-SY On-Line Mass Spec Tank Gas Composition



ON-LINE MASS SPEC SPECTRA

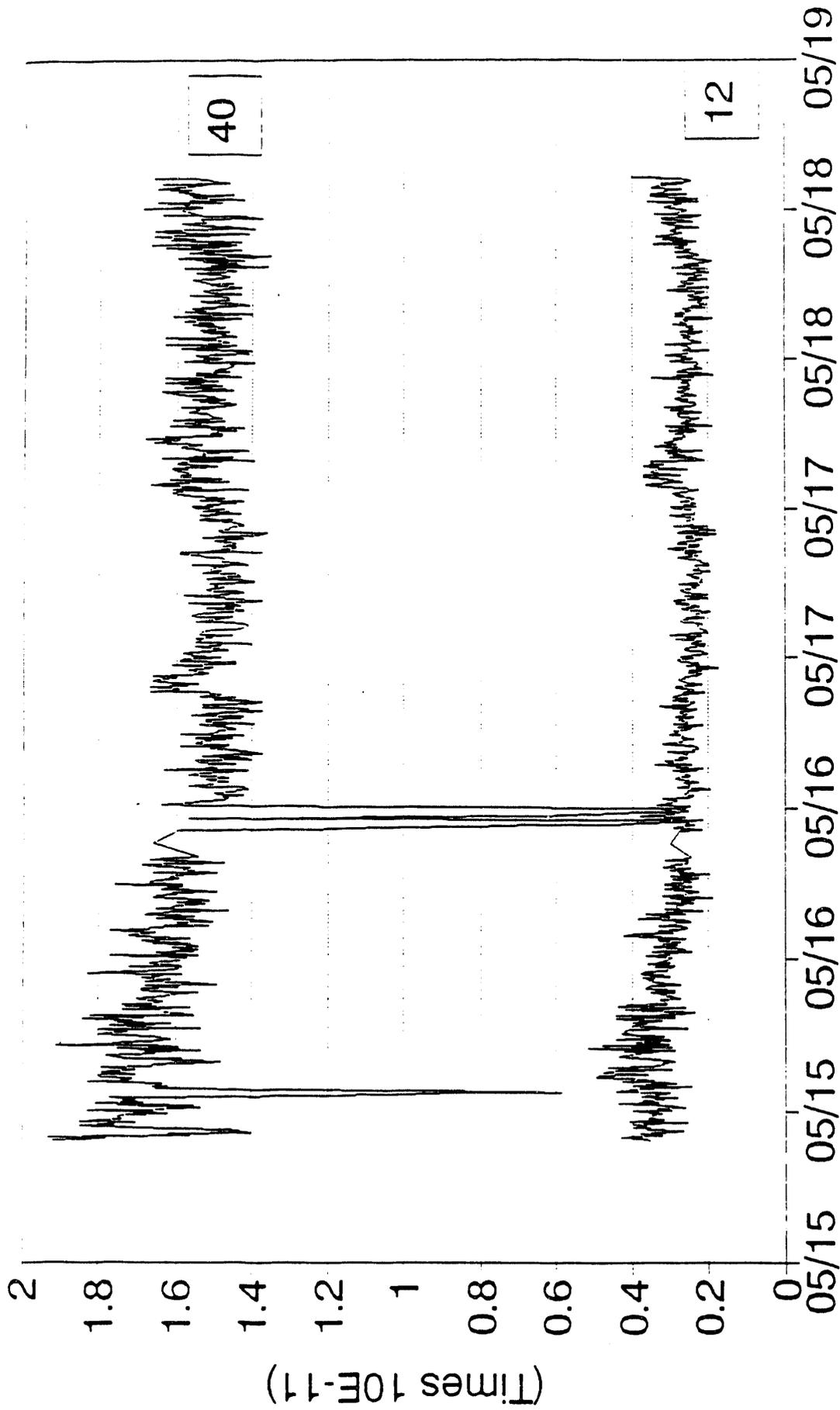


ON-LINE MASS SPEC



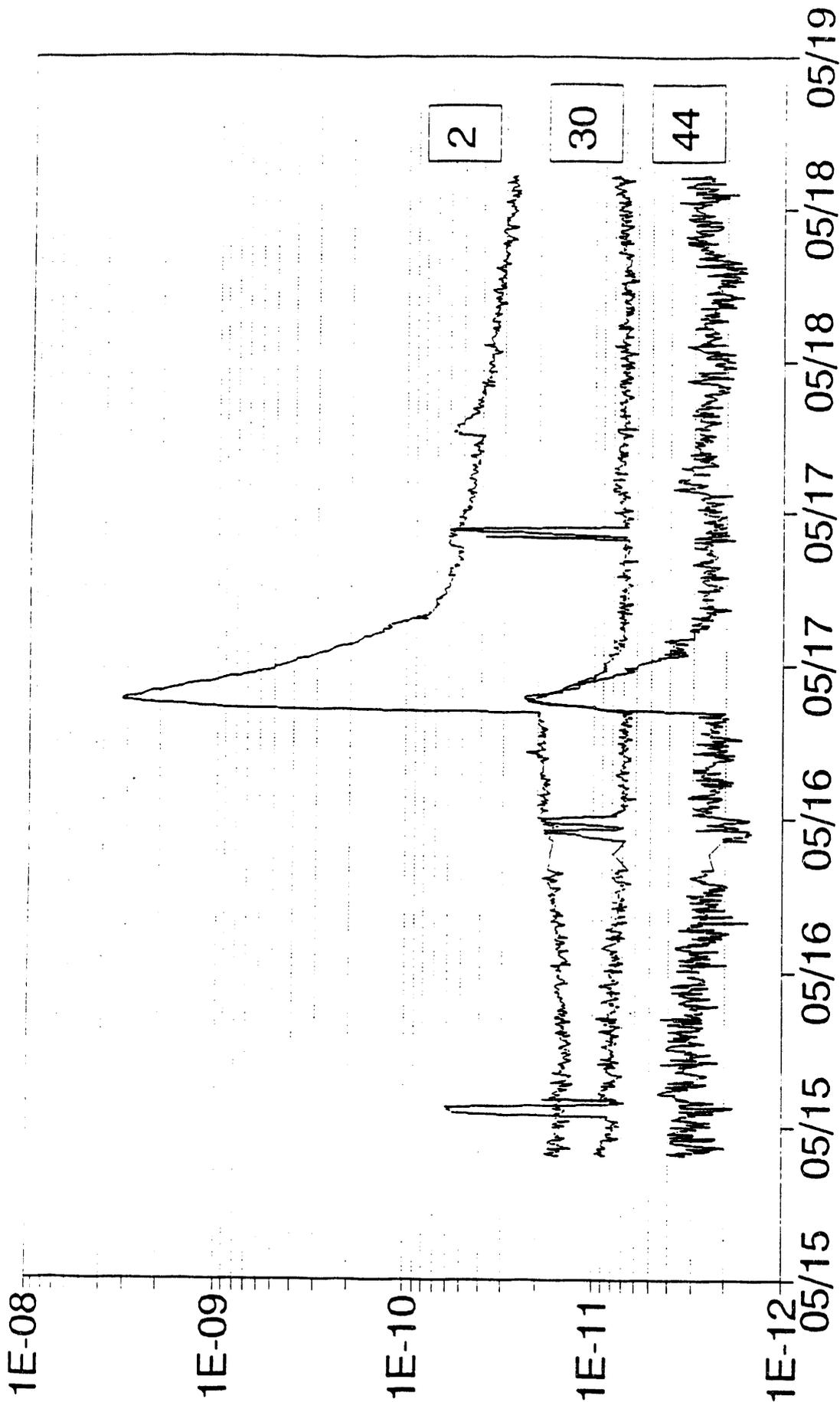
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ON-LINE MASS SPEC

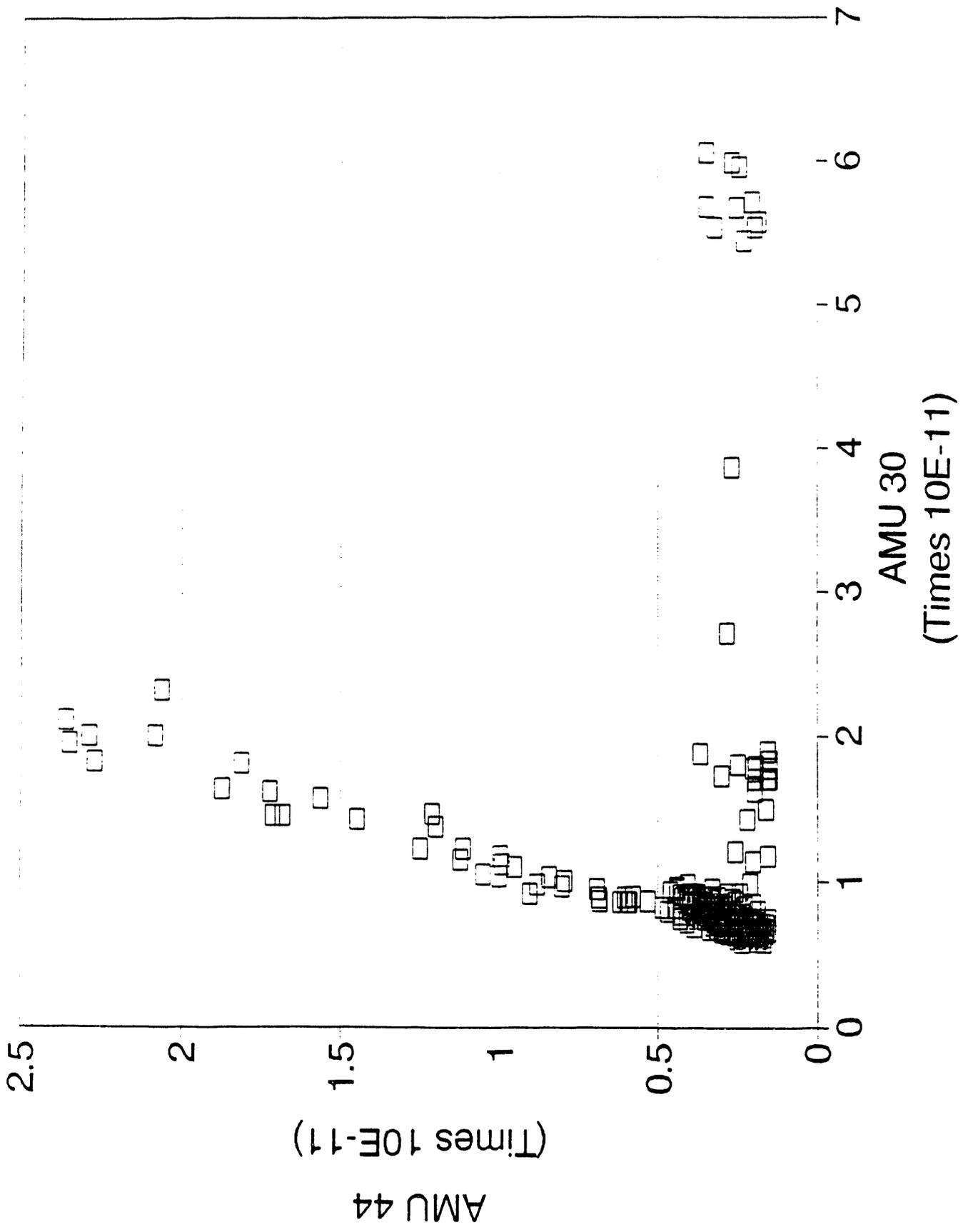


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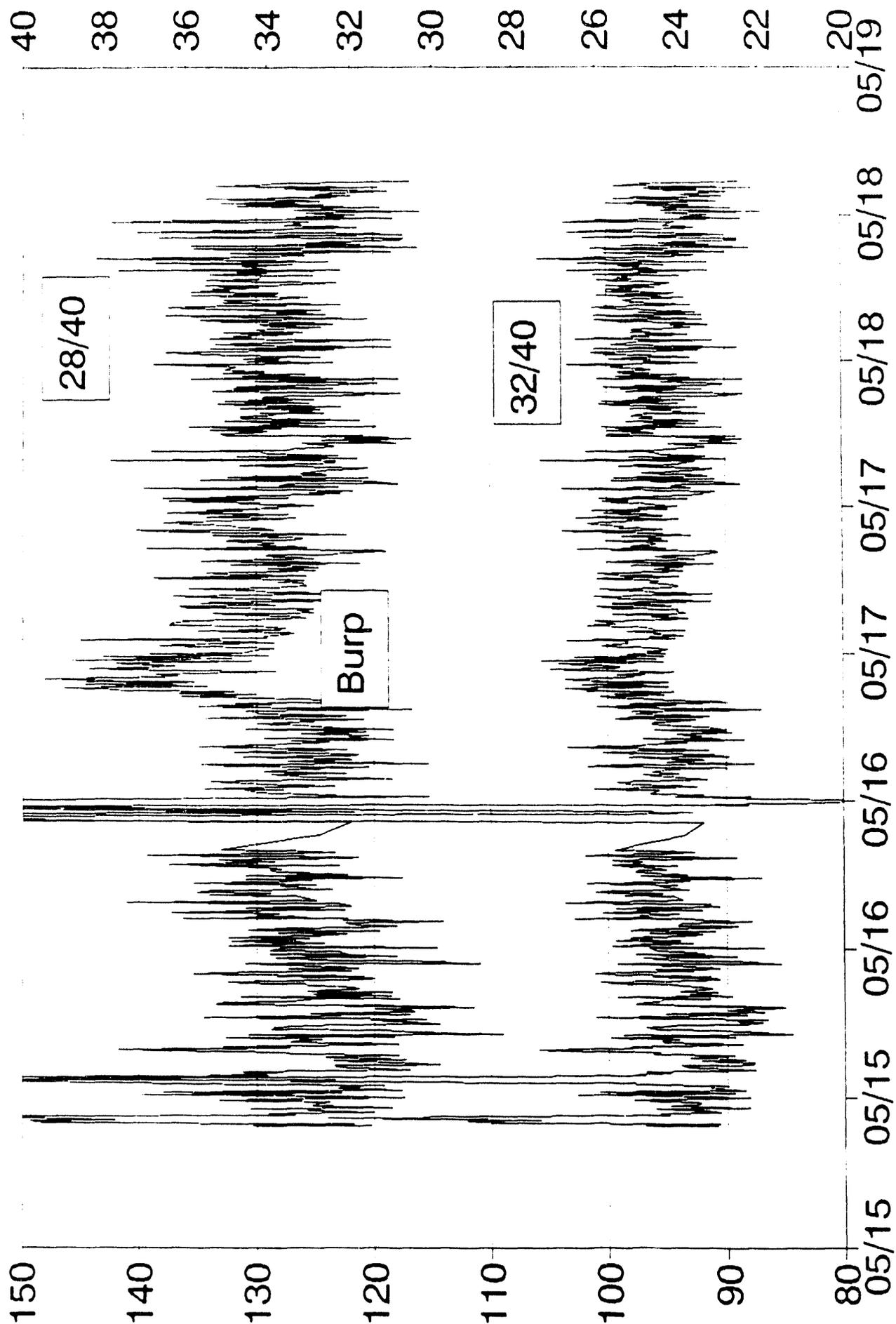
ON-LINE MASS SPEC SPECTRA



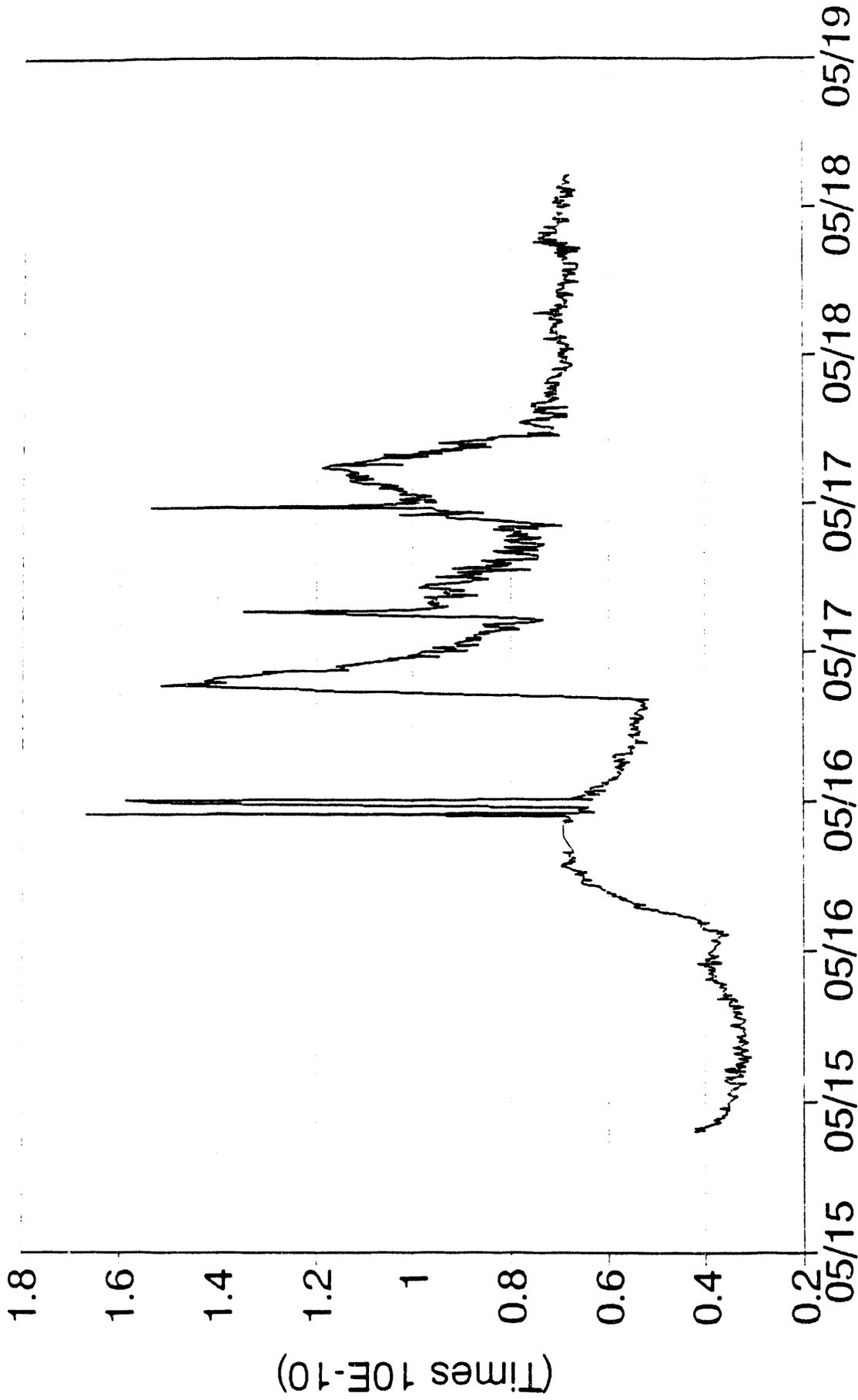
ON-LINE MASS SPEC SPECTRA



ON-LINE MASS SPEC SPECTRA

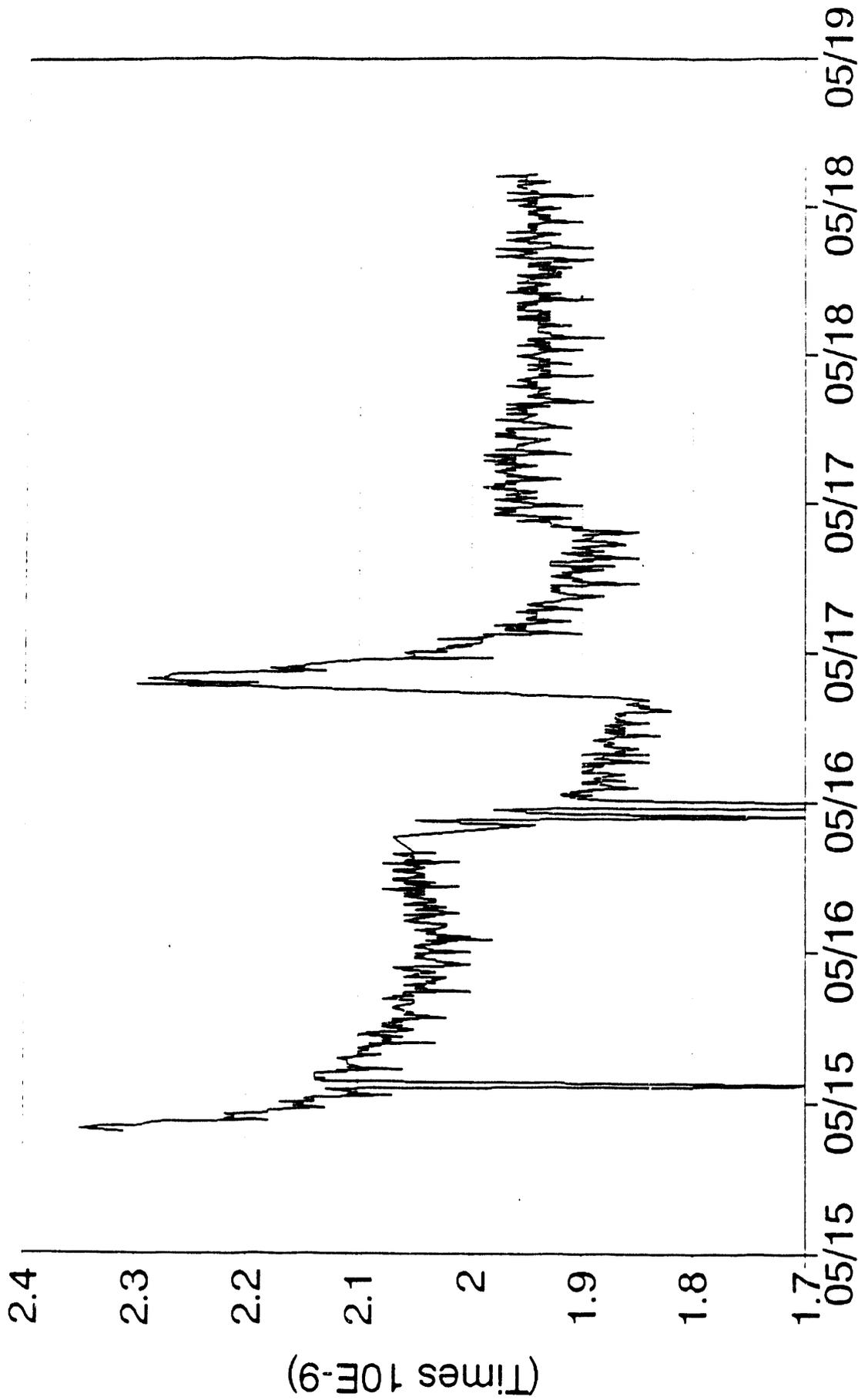


ON-LINE MASS SPEC SPECTRA



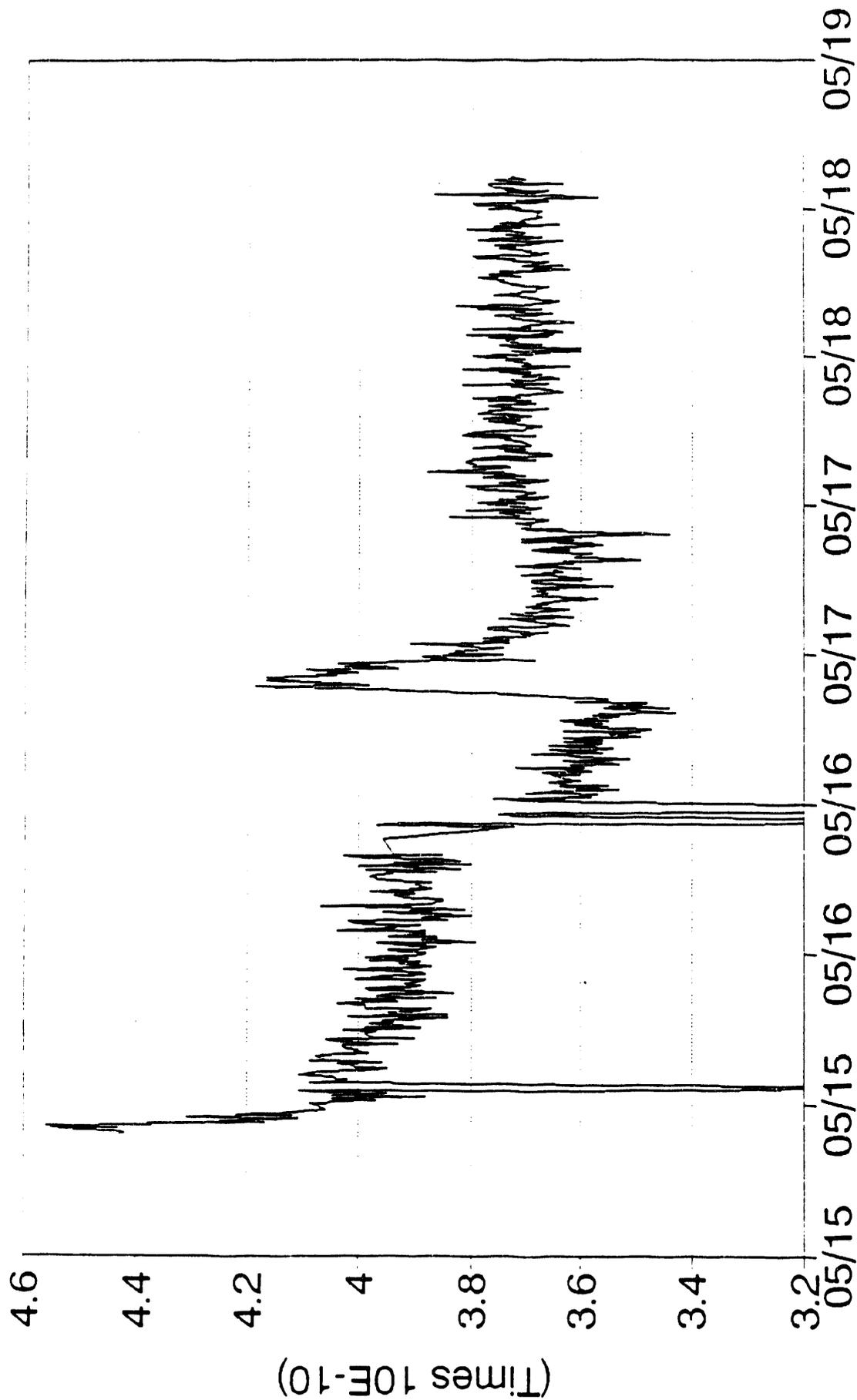
--- AMU 18

ON-LINE MASS SPEC SPECTRA



— AMU 28

ON-LINE MASS SPEC SPECTRA



SUMMARY

- **Indications are that a flammable gas mixture is present in waste**
- **Additional work needs to be done to work out the differences between methods.**

Appendix E

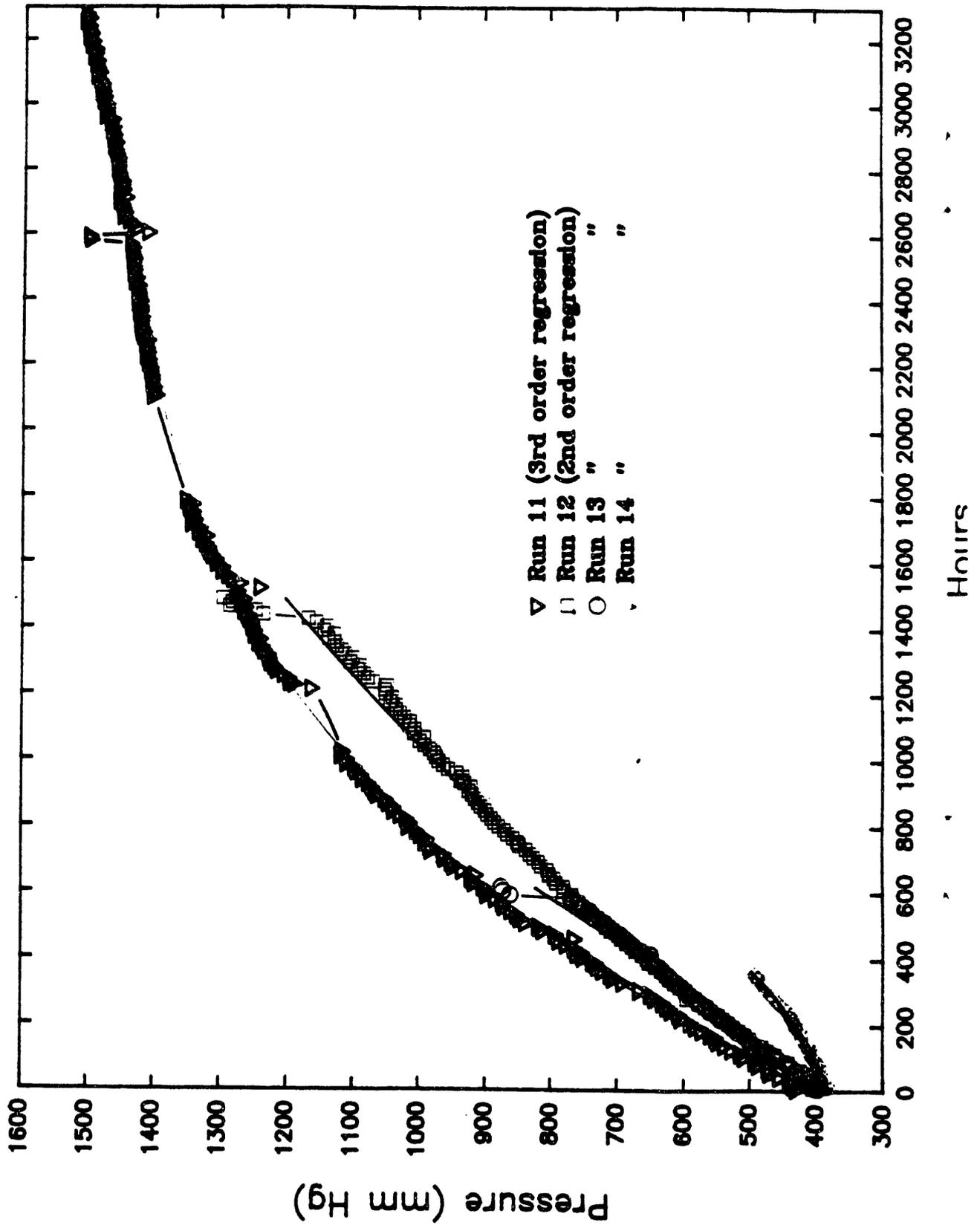
Gas Generation Studies

GAS GENERATION STUDIES

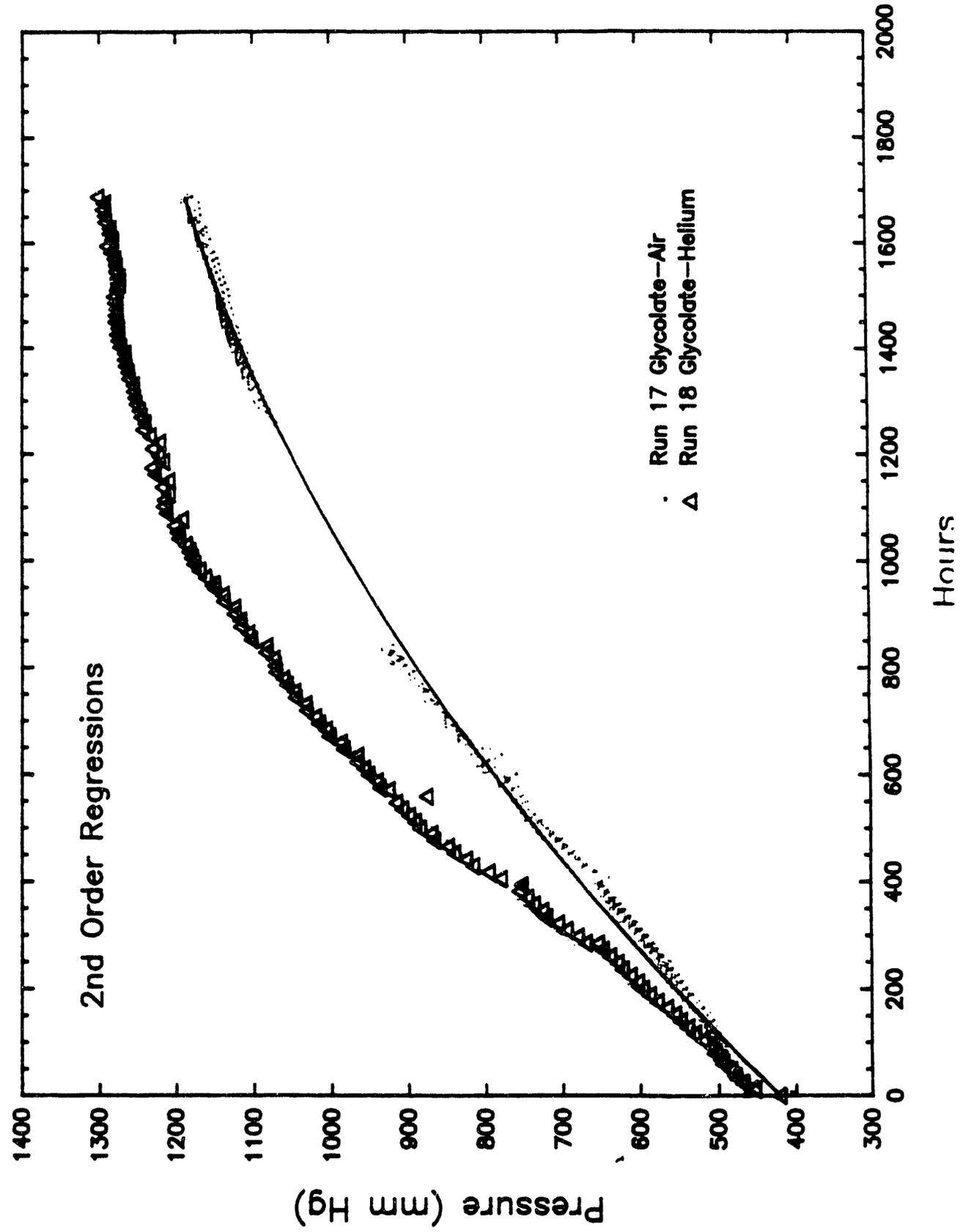
Daniel A. Reynolds, WHC

Data From Daniel Herting, WHC

HEDTA in Teflon under Air



Synthetic 101-SY with Glycolate under Helium and Air



SYNTHETIC GAS COMPOSITION

H2 N2 N2O NH3 N2O/H2 EXPERIMENT

3.2 35.3 57.5 3.8 17.8 HEDTA with air

2.1 20.4 50.9 3.6 24.3 HEDTA with He

48.8 -4.0 51.7 3.3 1.1 Glycolate with air

2.6.3 0.7 70.8 2.2 2.7 Glycolate with He

Appendix F

101-SY Synthetic Waste Studies

101-SY Synthetic Waste Studies

presented to

Tank Waste Science Panel
Richland, WA

by

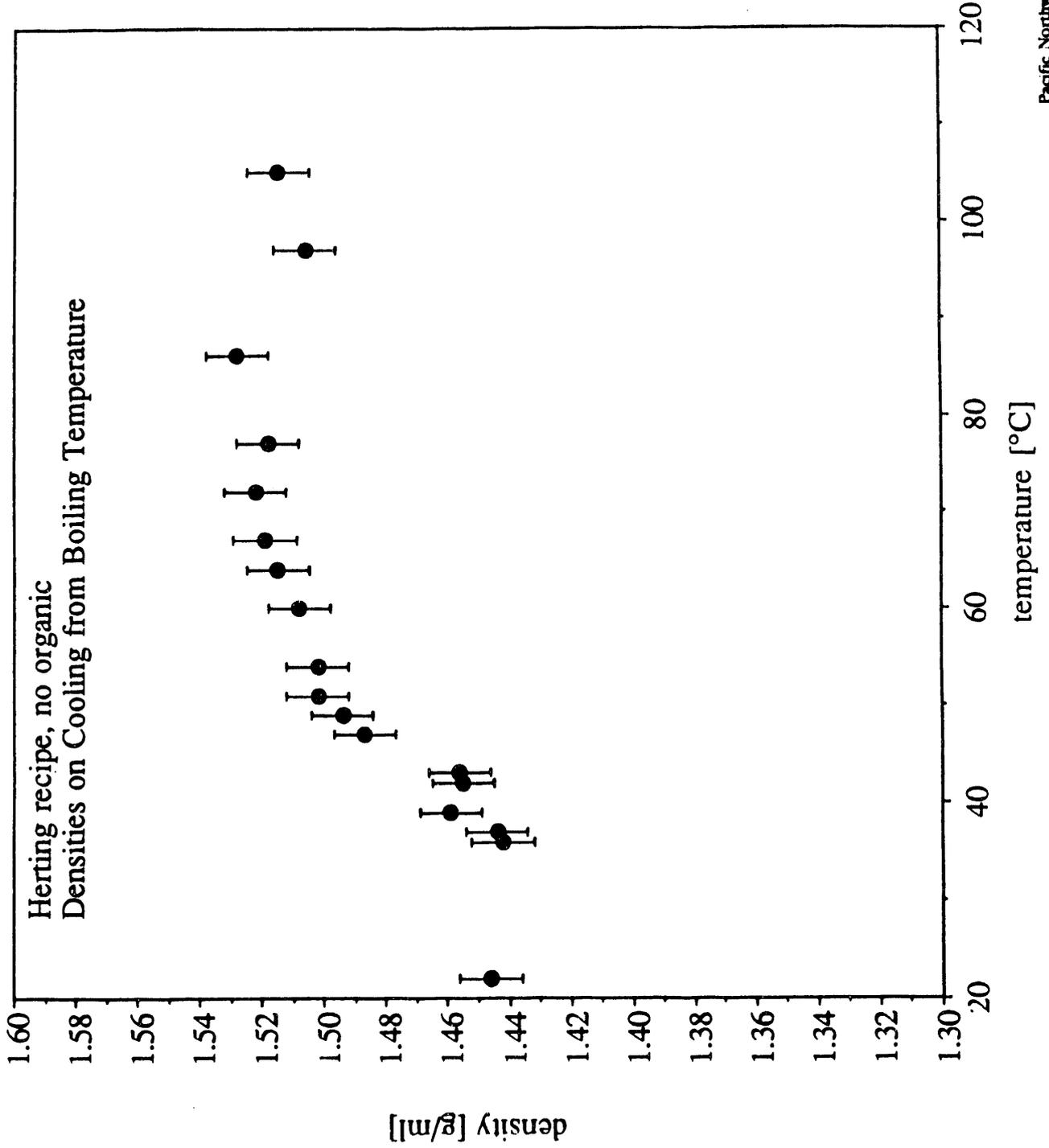
S. A. Bryan and L. R. Pederson
Pacific Northwest Laboratory
November 11-13, 1991

Topics to be Covered

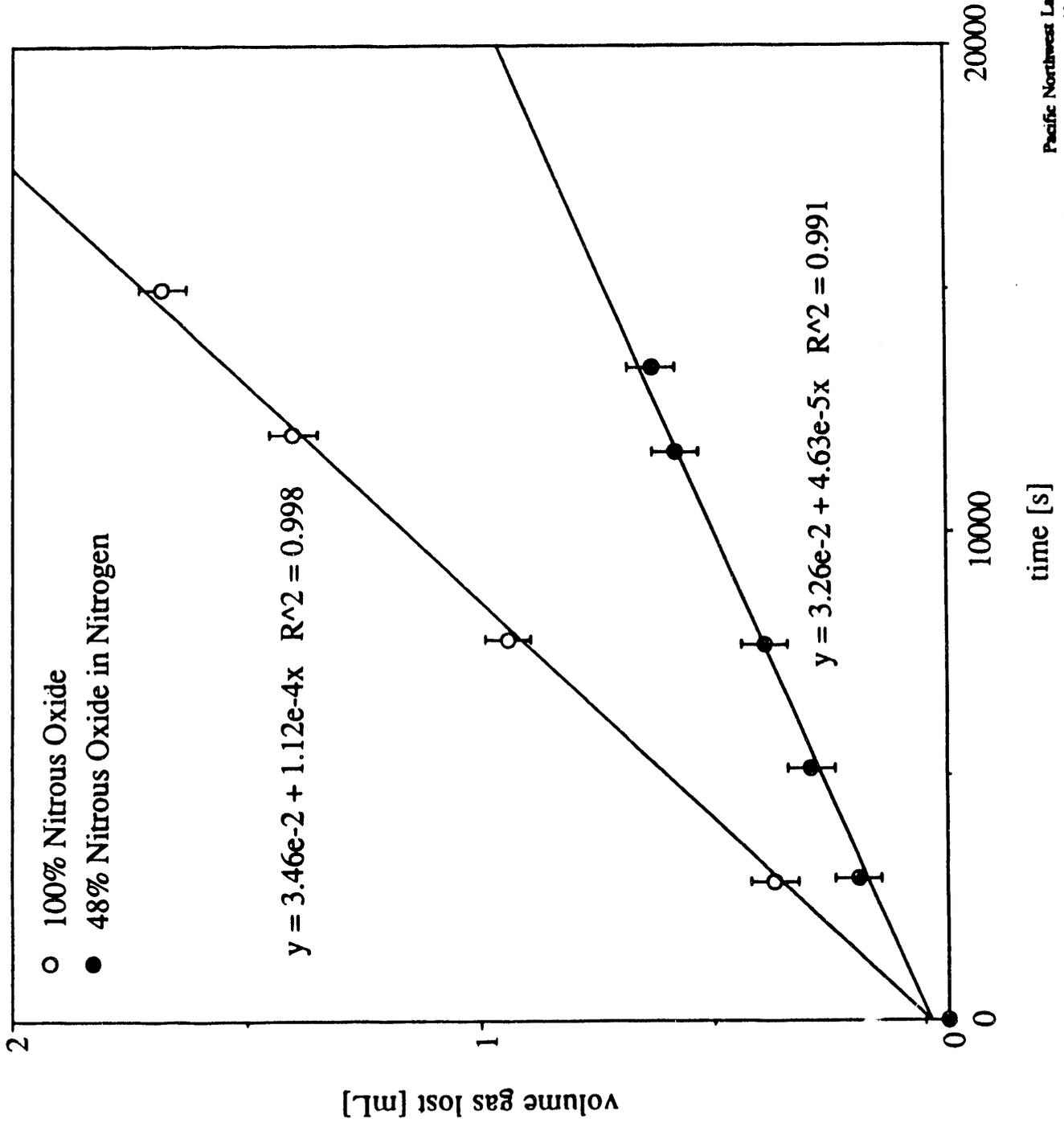
- Chemo-Physical Studies of Gas Retention
 - Density dependence on temperature
 - Nitrous oxide transport
 - Contact angle measurements
 - Surface tension measurements

- Integrated Gas Generation
 - Production of gases by thermolysis, radiolysis
and iron corrosion

Density Changes in Synthetic Waste as a Function of Temperature



Rate of Nitrous Oxide Transport Through a Water Column (0.6 inch dia., 37 in. long)



F.4

Contact Angles and Gas Bubble Retention

$$\cos \theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV}$$

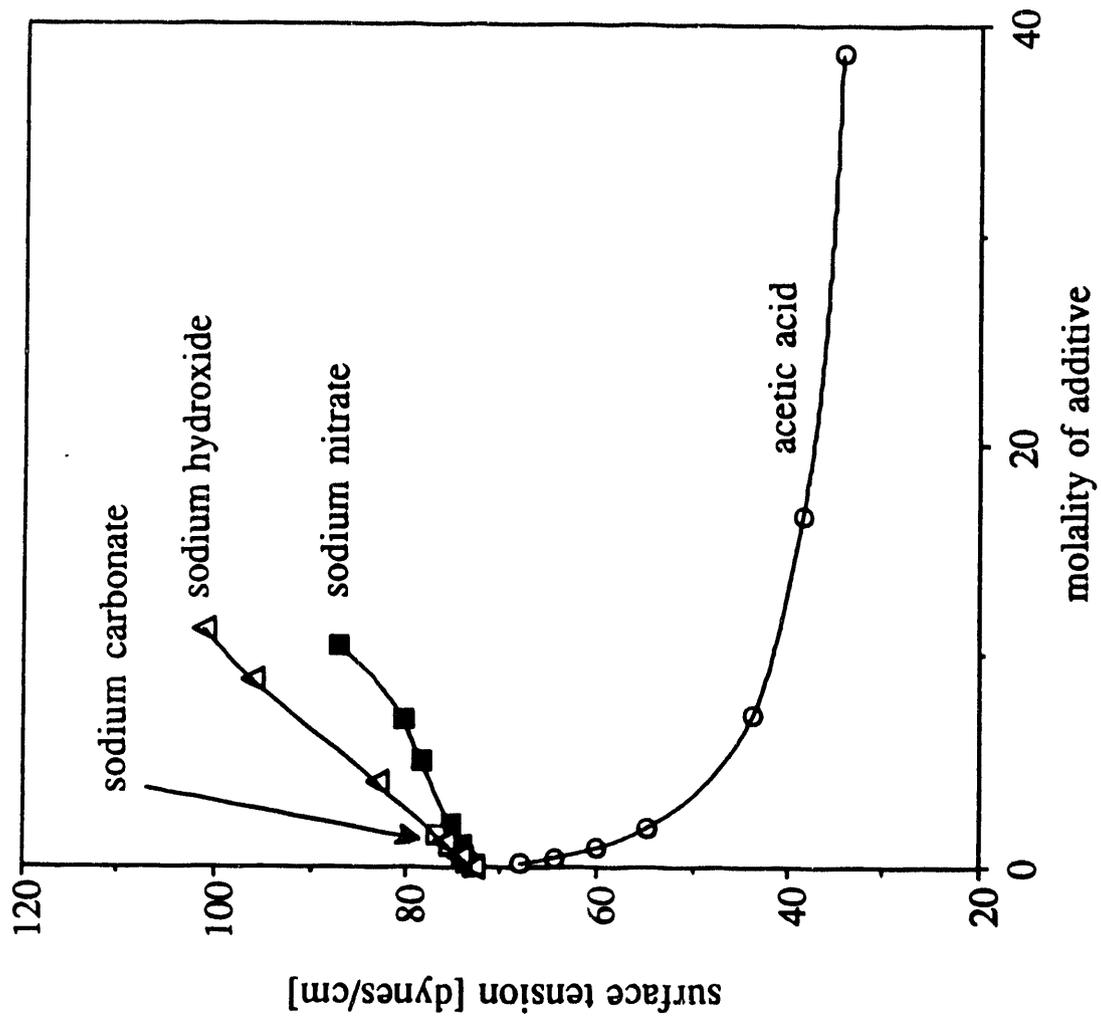
High contact angles result in enhanced gas retention

The term $\sigma_{SV} - \sigma_{SL}$ is strongly affected by surface adsorption of organic waste components

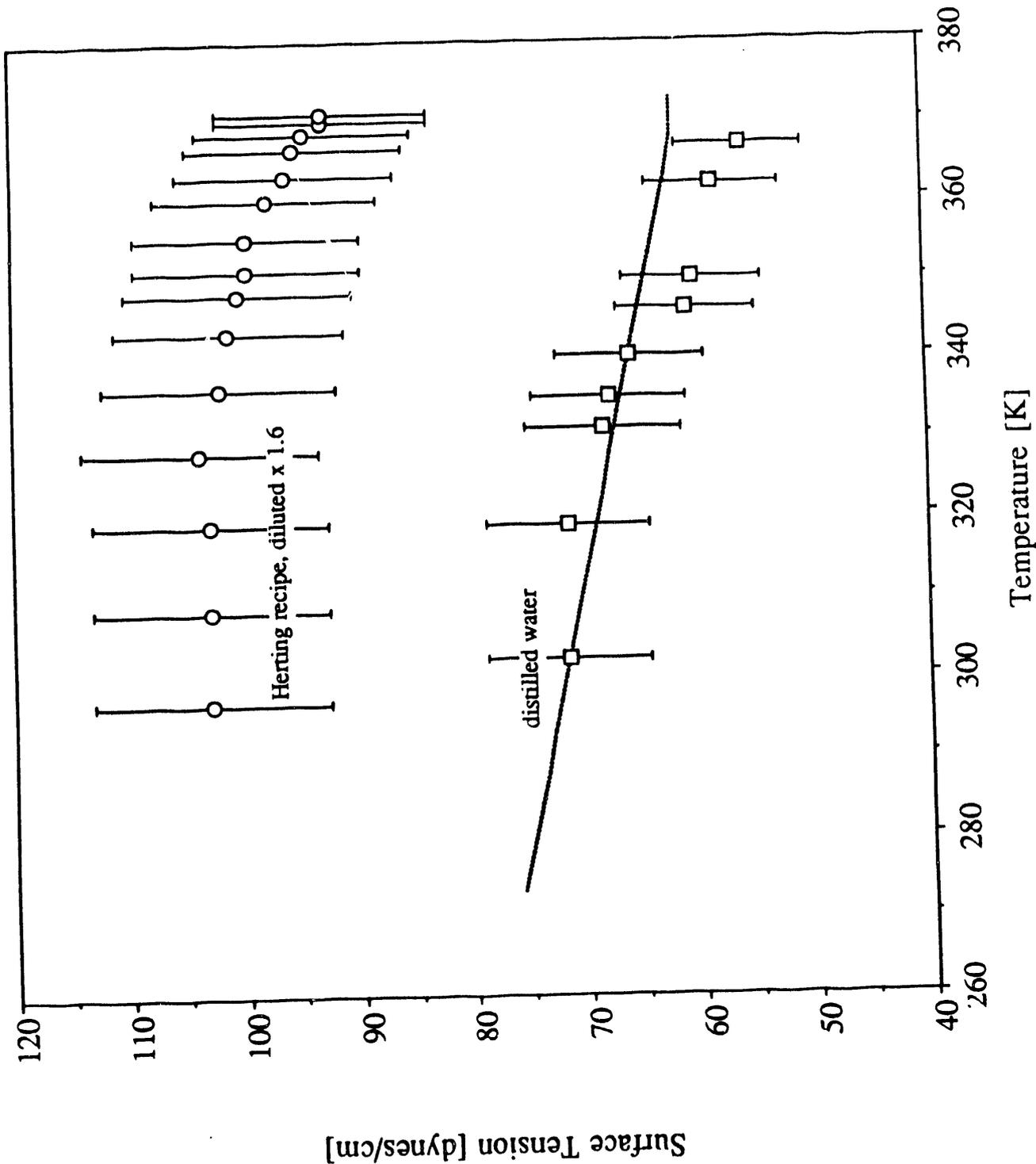
The term σ_{LV} decreases slowly with temperature
increases with electrolyte concentration
decreases with organic concentration

Pacific Northwest Laboratory
Tank Waste Science Panel Meeting, November 11-13, 1991

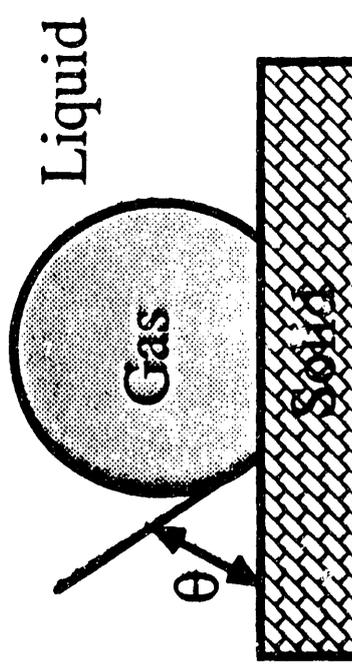
Literature Surface Tension Data



Surface Tension Versus Temperature

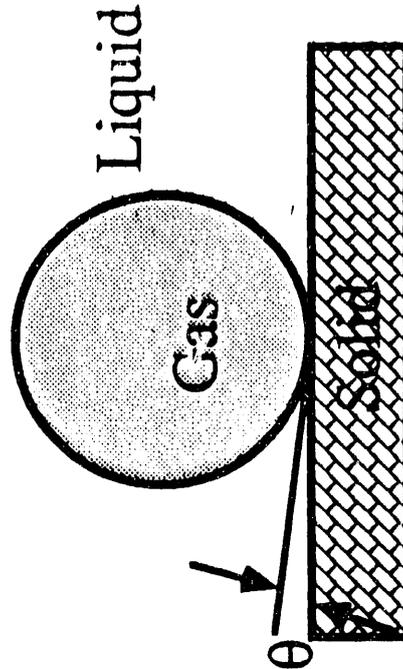


Adsorption of Organic Waste Components Lowers The Wettability of Solids, Enhances Gas Bubble-Particle Adhesion



The diagram shows a circular gas bubble on a hatched solid surface. The contact angle θ is large, indicating poor wettability. Labels 'Liquid' and 'Gas' are positioned above the bubble. The solid surface is labeled 'Solid'.

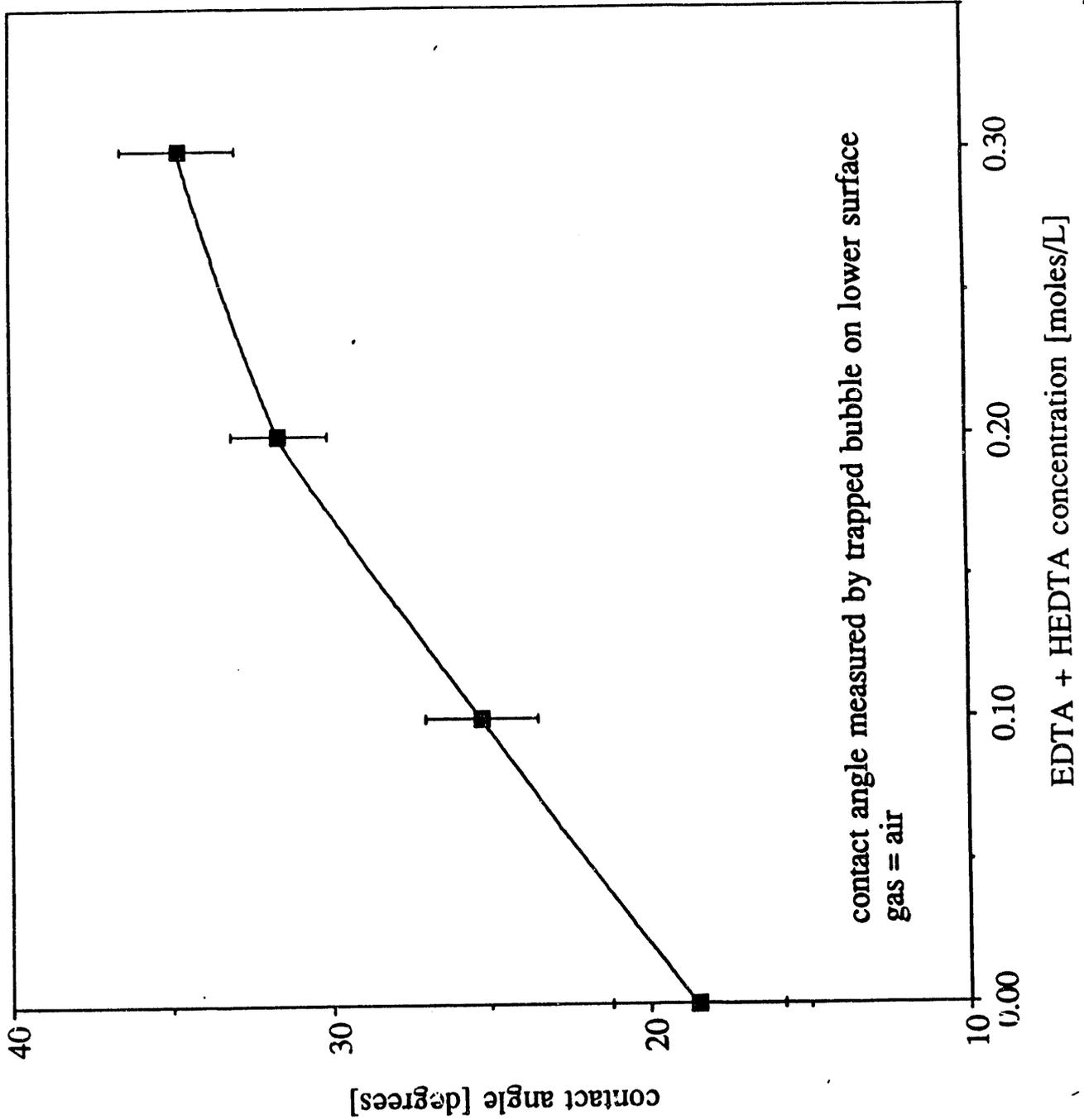
**Organics Present
Reduced Solids Wettability
Gas Bubble Retention**



The diagram shows a circular gas bubble on a hatched solid surface. The contact angle θ is small, indicating high wettability. Labels 'Liquid' and 'Gas' are positioned above the bubble. The solid surface is labeled 'Solid'.

**Organics Absent
Nearly Complete Wetting
Little or No Bubble Retention**

Contact Angle on Sapphire versus Complexant Concentration in Synthetic Waste



Topics to be Covered

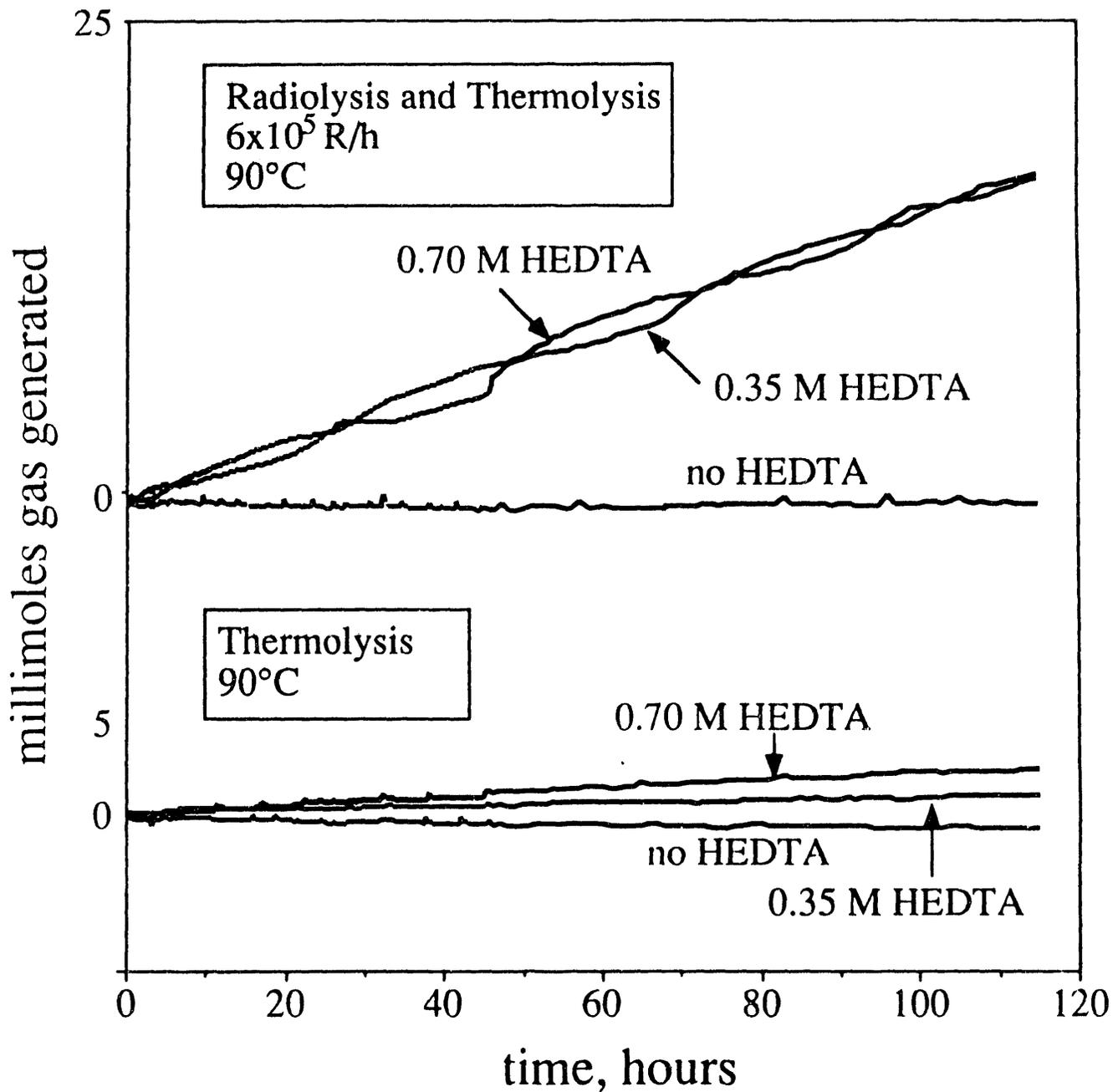
- Chemo-Physical Studies of Gas Retention

 - Density dependence on temperature
 - Nitrous oxide transport
 - Contact angle measurements
 - Surface tension measurements

- Integrated Gas Generation

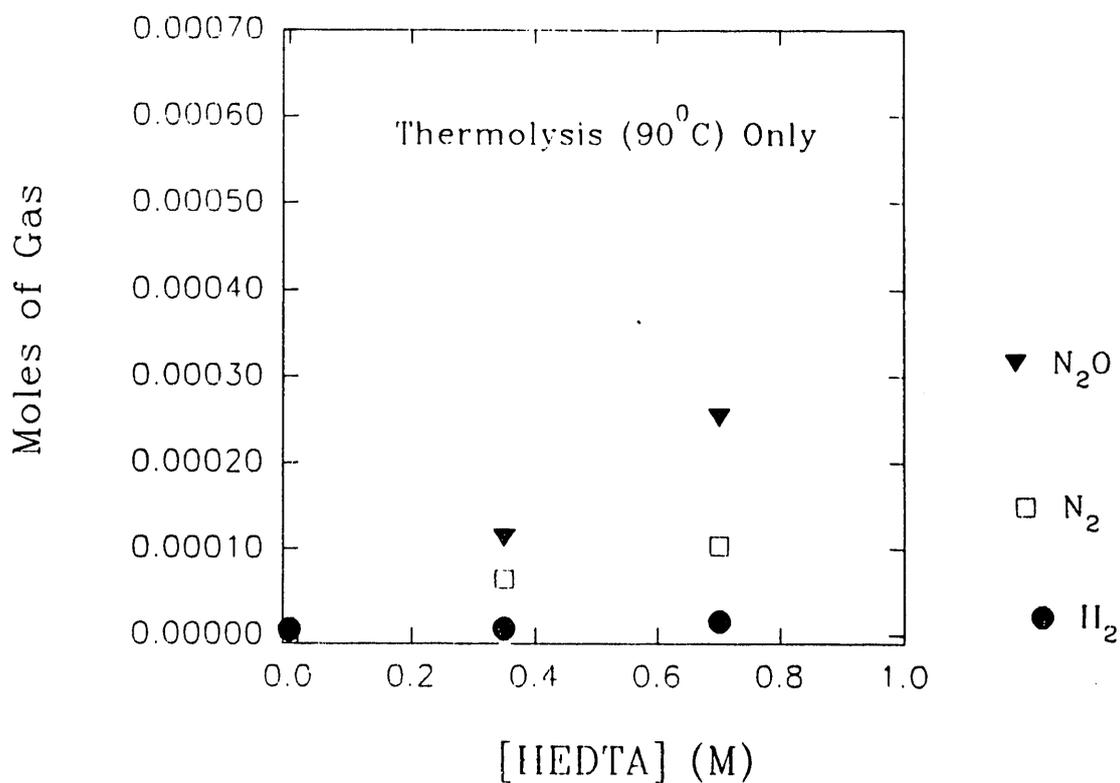
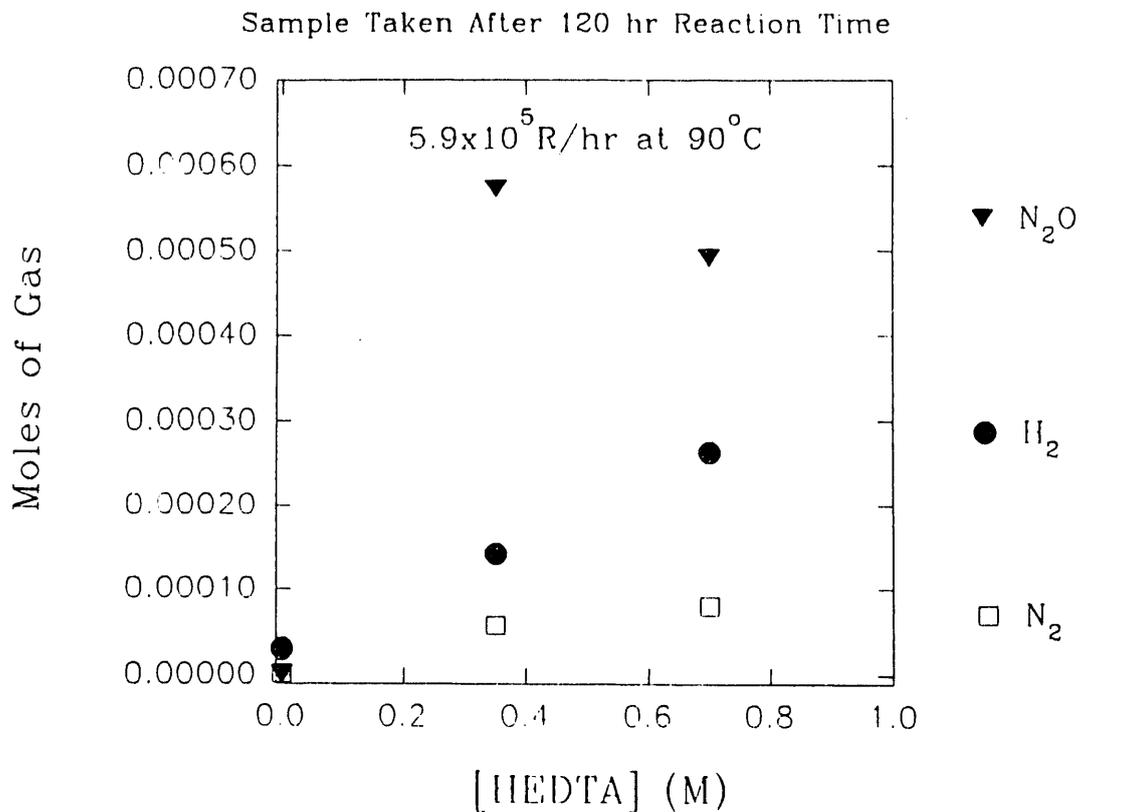
 - Production of gases by thermolysis, radiolysis
and iron corrosion

Radiolysis: Organic Needed But Insensitive to Concentration
Thermolysis: Rate Depends on Organic Concentration



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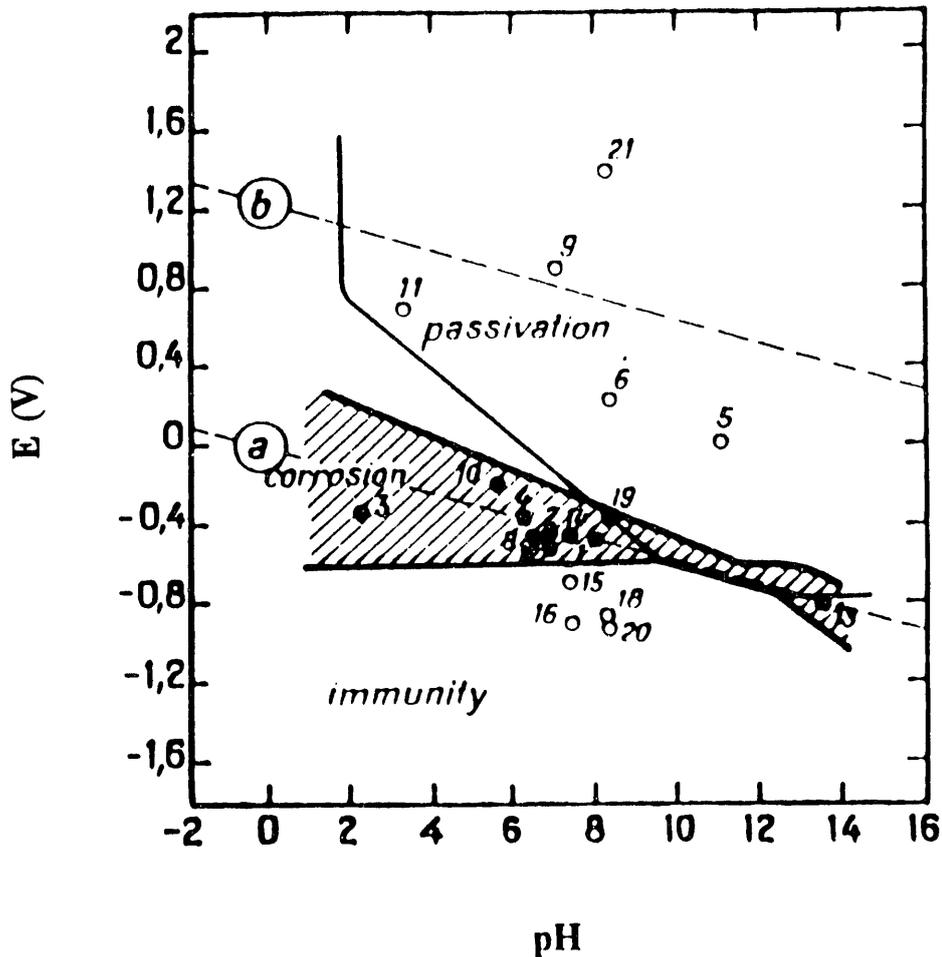
Gaseous Products from Thermal and Radiolytic Reactions



Laboratory Estimates for Hydrogen Generation Similar to Actual Tank Observations; Large Discrepancy for Nitrous Oxide

	Hydrogen	Nitrous Oxide
Tank 101-SY Estimates	60	50
Thermolysis	20	100
Radiolysis	20	200
Tank Wall Corrosion	6	-
		(cubic feet per day)

Theoretical and Experimental Conditions of Corrosion and non-Corrosion of Iron

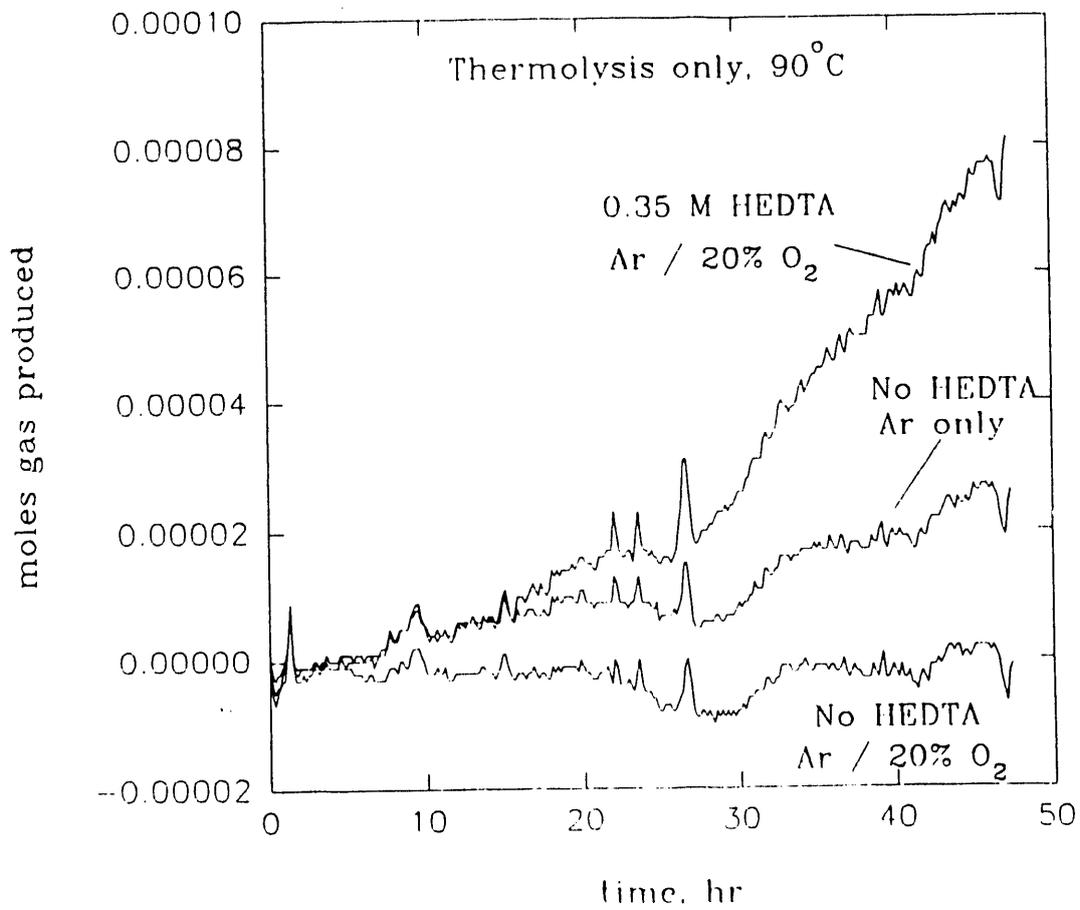


No. 5 NaOH, 0.03M; pH = 11.2; $E(V) = +0.026$; non-corrosive
 No. 13 Air free NaOH, 1.0M; pH = 13.7; $E(V) = -0.810$; corrosive

"Atlas of Electrochemical Equilibria in Aqueous Solutions" M. Pourbaix

Pacific Northwest Laboratory
 Tank Waste Science Panel Meeting, November 11-13, 1991

Synthetic Waste with 5g Fe



Pacific Northwest Laboratory
Tank Waste Science Panel Meeting, November 11-13, 1991

Moles of Gas Generated in Thermal Reactions

25g Synthetic Waste, 0.35M HEDTA, 90°C

	N ₂	H ₂	N ₂ O
Fe added*	2.19 x 10 ⁻⁵	5.85 x 10 ⁻⁶	4.28 x 10 ⁻⁵
No Fe added	2.44 x 10 ⁻⁵	2.64 x 10 ⁻⁶	4.24 x 10 ⁻⁵

* 5g - 100 mesh electrolytic iron

Summary of Experimental Results

- Physical parameters pertinent to the understanding of gas retention have been measured
 - Synthetic waste supernate density increases with increasing temperature
 - The rate of transport of nitrous oxide across a water membrane is directly related to the partial pressure of N_2O
 - The surface tension of synthetic waste decreases with increasing temperature
 - Contact angles increase as organic complexant concentration is increased in synthetic wastes

Summary of Experimental Results

• Gas generation has been measured in complex simulated waste systems

Thermal

- Organic required for gas production with Ar/O₂ cover gas
- Rate of production of H₂, N₂, and N₂O depends on organic concentration
- Organic not needed for gas generation with added iron in the absence of O₂
- Hydrogen is the product of iron corrosion in the synthetic waste formulation

Radiolytic

- Organic needed but total gas generation insensitive to concentration of organic
- Production of H₂ and N₂O are both enhanced in gamma field
- N₂ production is insensitive to radiolysis

Appendix G

Radiolytic Generation of Gases from Synthetic Waste

Task Force on
"RADIOLYTIC GENERATION OF GASES FROM SYNTHETIC
WASTE"

Chemistry Division
Argonne National laboratory

D. (Dani) Meisel	(El. Transfer & Energy Conversion Group)
H. (Herb) Diamond	(Separations Group)
E. P. (Phil) Horwitz	(Separations Group)
C. (Chuck) D. Jonah	(Radiation Chemistry Group)
Max S. Matheson	(El. Transfer & Energy Conversion Group)
Myran C. Sauer	(Radiation Chemistry Group)
Jim (Sully) C. Sullivan	(Heavy Elements Group)
Freddy Barnabas	(Task Force Personnel)
Beth Cerny	(Task Force Personnel)
Yuan Di Cheng	(Task Force Personnel)
Yori Wojta	(Task Force Personnel)

WHC-DOE/RL funding

Many Years of DOE-BES support

Radiolytic Gas Formation in High-level Liquid Waste Solutions*

Bert-G. Brodda, Siegfried Dix and Erich R. Merz
 Institute of Chemical Technology, Nuclear Research Centre Jülich GmbH, D-5170 Jülich, FRG

High-level fission product waste solutions originating from the first-cycle raffinate stream of spent fast breeder reactor fuel reprocessing have been investigated gas chromatographically for their radiolytic and chemical gas production. The solutions showed considerable formation of hydrogen, carbon dioxide and dinitrogen oxide, whereas atmospheric oxygen was consumed completely within a short time, in particular carbon dioxide resulted from the radiolytic degradation of an irradiated organic solvent. After nearly complete degradation of the organic solvent, the influence of hydrazine and nitrogen dioxide on hydrogen formation was investigated. Hydrazinium hydroxide led to the formation of dinitrogen oxide and nitrogen. After 60 d, the concentration of dinitrogen oxide had reduced to zero, whereas the amount of nitrogen formed had reached a maximum. This may be explained by simultaneous chemical and radiolytic reactions leading to the formation of dinitrogen oxide and nitrogen and photolytic fission of dinitrogen oxide. Addition of sodium nitrite resulted in the rapid formation of dinitrogen oxide. The rate of hydrogen production was not changed significantly after the addition of hydrazine or nitrite. The results indicate that under normal operating conditions no dangerous hydrogen radiolysis yields should develop in the course of reprocessing and high-level liquid waste tank storage. Organic entrainment may lead to enhanced radiolytic decomposition and thus to considerable hydrogen production rates and pressure build-up in closed systems.

Keywords: Spent reactor fuel reprocessing; high-level fission product waste solution; radiolysis; radiolytic gas formation; gas chromatography

High-level liquid waste (HLLW) solutions originating from spent nuclear fuel reprocessing undergo radiolytic degradation, the characteristics of which depend on numerous factors. These concern the energy distribution of the α -, β - and γ -radiation present in the solution, the energy dose absorbed by the solution, the composition of the solution with regard to the presence of salts, nitric acid and organic material, the temperature of the stirred or non-stirred solution and the geometric conditions of the container holding the solution.

The most important gaseous radiolysis product is clearly hydrogen because of the explosion hazards of oxidant-containing gas mixtures with more than about 4% V/V of hydrogen. Hydrogen is formed radiolytically by a number of reactions during Purex reprocessing in the dissolver, feed adjustment and solvent-extraction units and in HLLW storage tanks. HLLW storage may potentially lead to the build-up of dangerous concentrations of hydrogen under non-normal operating conditions such as a malfunction of the ventilation system.

A large number of relevant investigations have been published. Literature reviews include detailed basic theories and facts about the fundamental effects of water radiolysis and discussion of the parameters mentioned earlier.^{1,2} Results from on-site measurements in HLLW tanks of a reprocessing facility have been reported³ and a comprehensive investigation of γ -radiolysis in fission product solutions has been described.⁴

All investigations show that radiolytically formed radical or ionic precursors of molecular hydrogen under normal operating conditions recombine to different harmless species before significant amounts of hydrogen are formed and released from the liquid phase. This applies especially in the presence of radical scavengers such as nitrates, which typically exist in high concentrations in Purex HLLW solutions.

Experimental and Results

Original HLLW Solution

About 2 years ago our laboratory received HLLW from reprocessing of fast breeder reactor fuel, performed in the

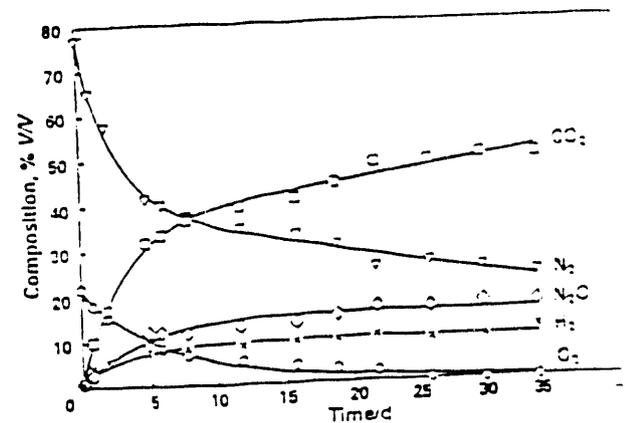


Fig. 2. Composition of high-level liquid waste radiolysis gas; initial atmosphere: air

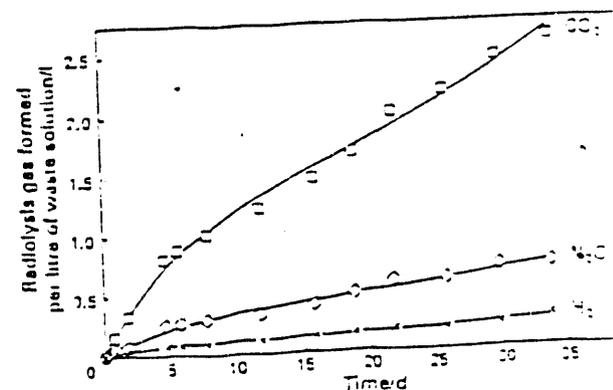


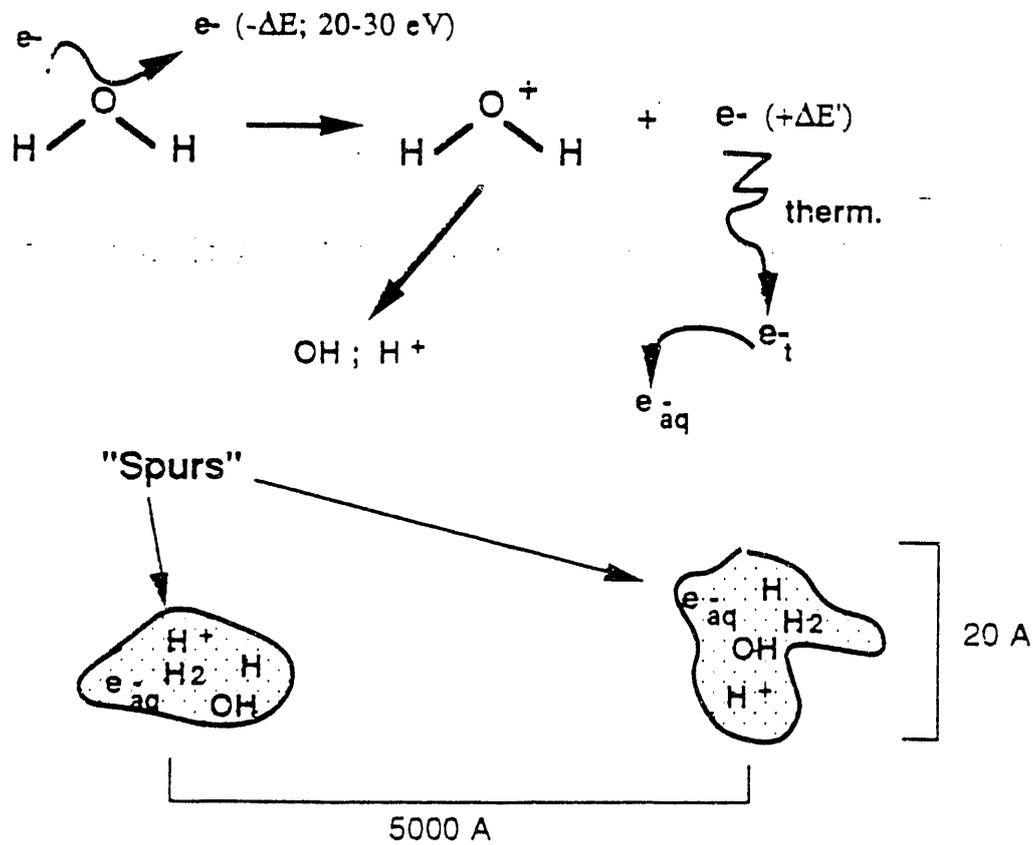
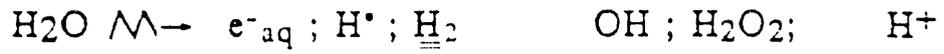
Fig. 3. Total radiolytic gas formation 1 year after receipt; initial atmosphere: air

^{238}Pu 0.02
 ^{239}Pu 6.4 $\times 10^{-2}$
 ^{240}Pu 3.9 $\times 10^{-2}$

- * Determined by gross β -measurement.
- Determined by α -spectrometry and X-ray fluorescence.
- ◊ Determined by α -spectrometry.

* Presented at the 2nd International Conference on Nuclear and Radiochemistry, Brighton, UK, 11-15 July, 1988.

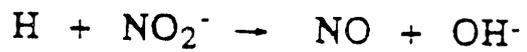
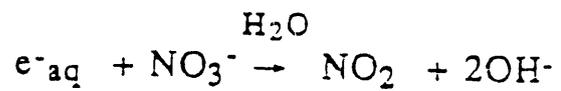
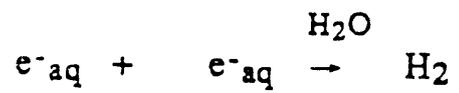
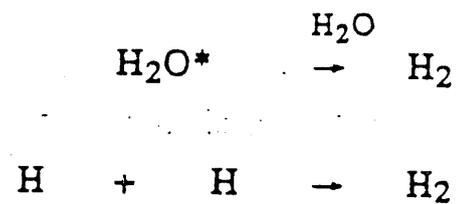
(γ or β Radiation)



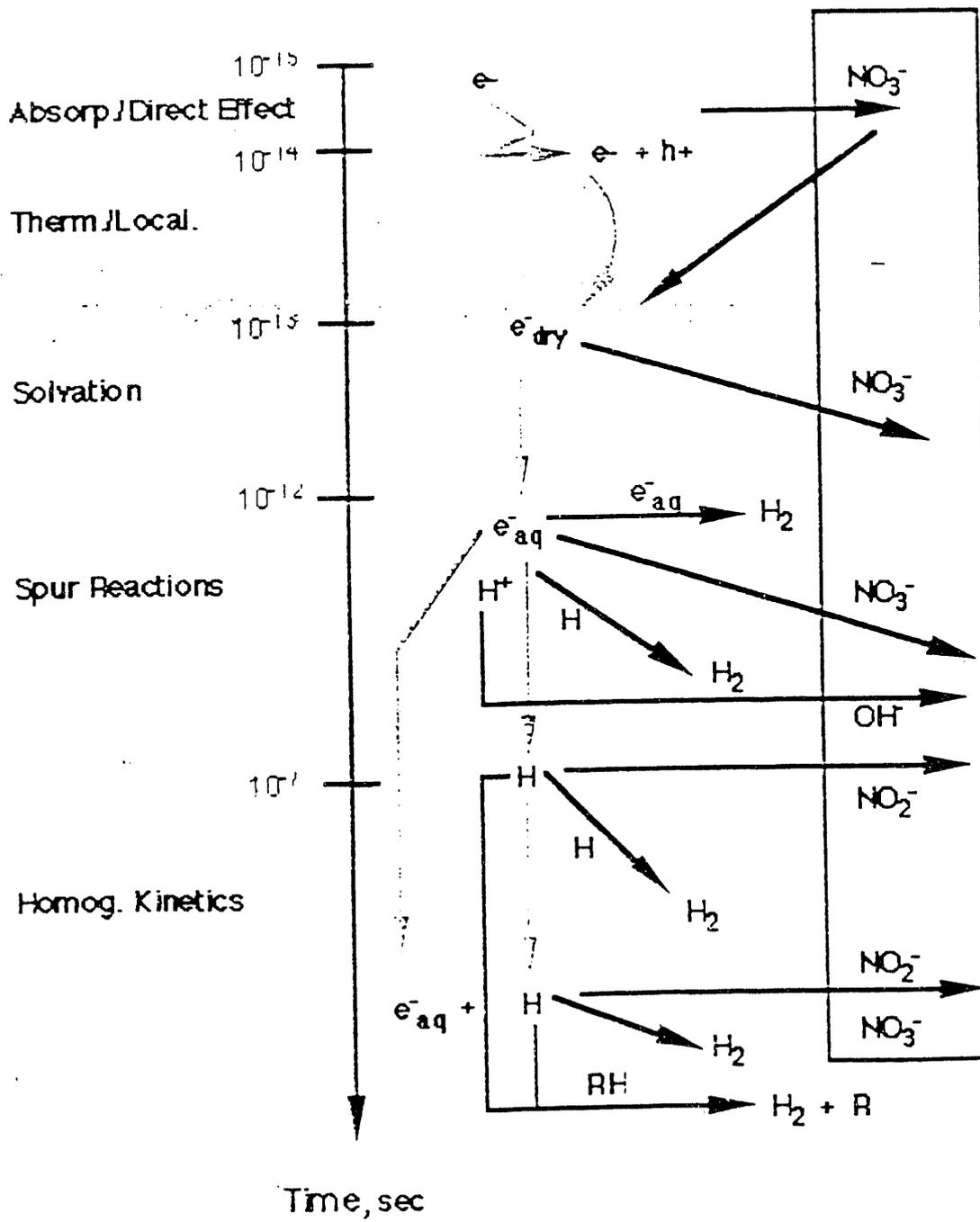
$$\frac{\partial [c_i]}{\partial t} = D_i \nabla^2 [c_i] - \sum_j k_{ij} [c_i] [c_j] + \sum_{j,k} k_{jk} [c_j] [c_k]$$

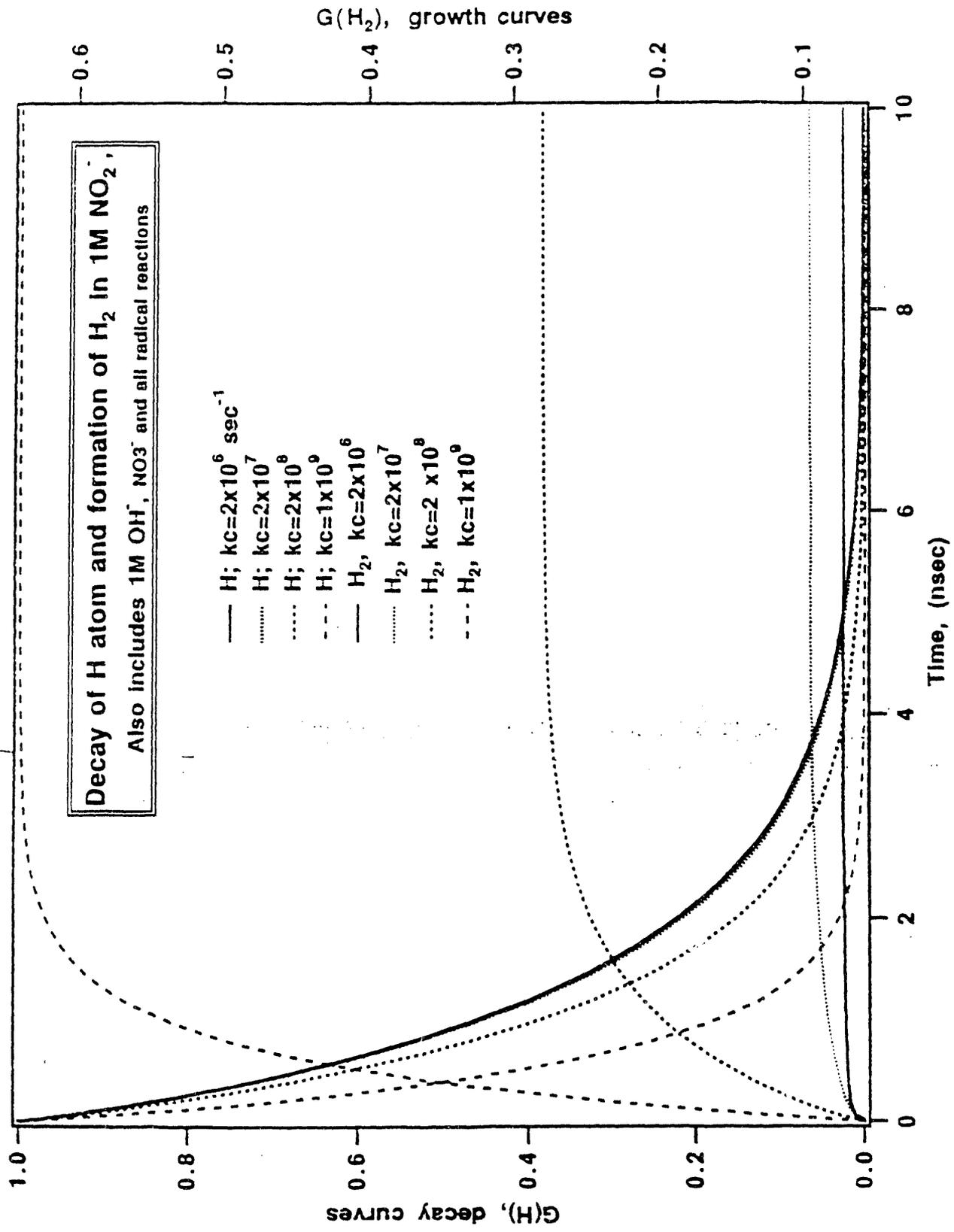
Hydrogen Generation Reactions

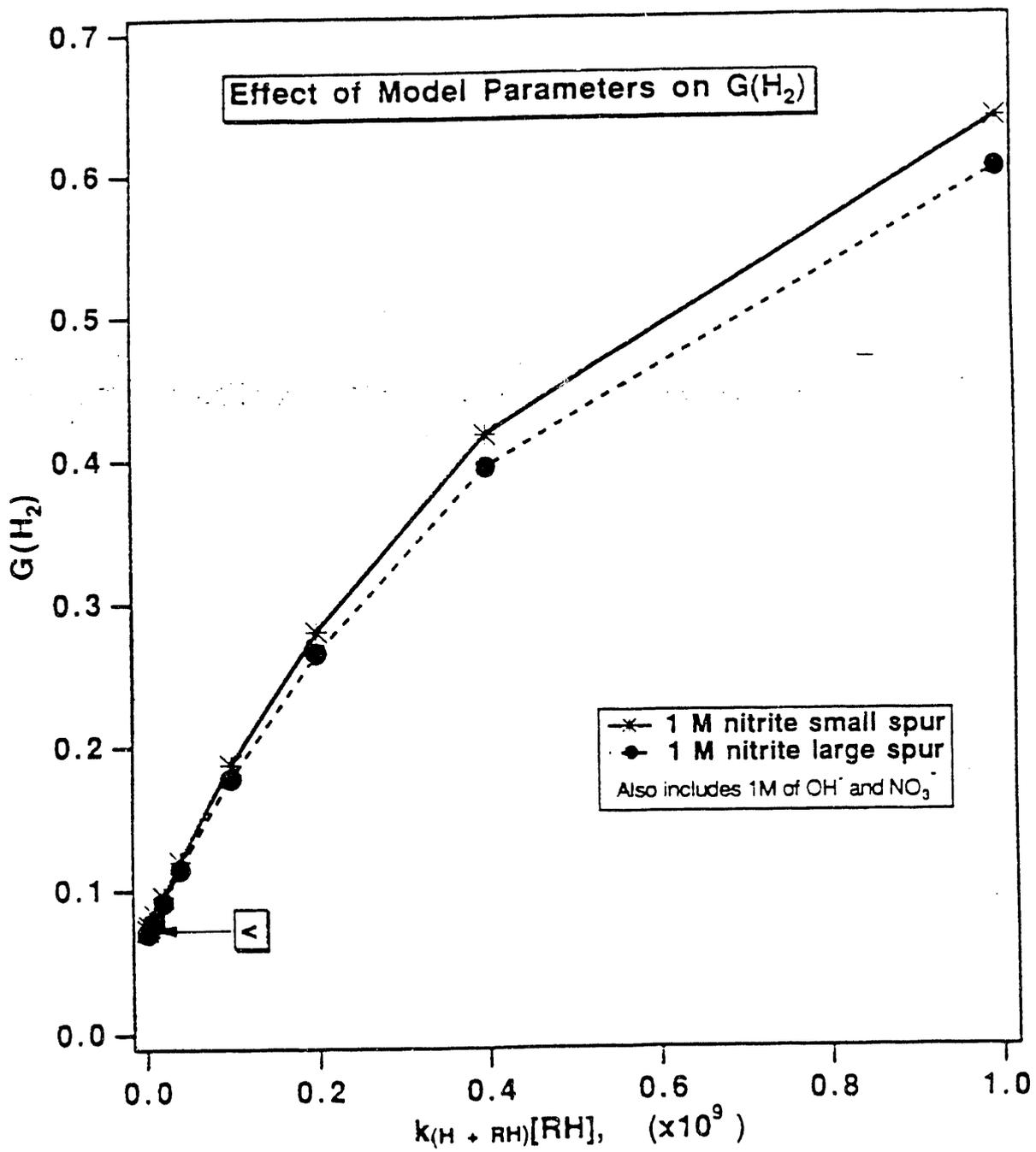
Hydrogen Averting Reactions



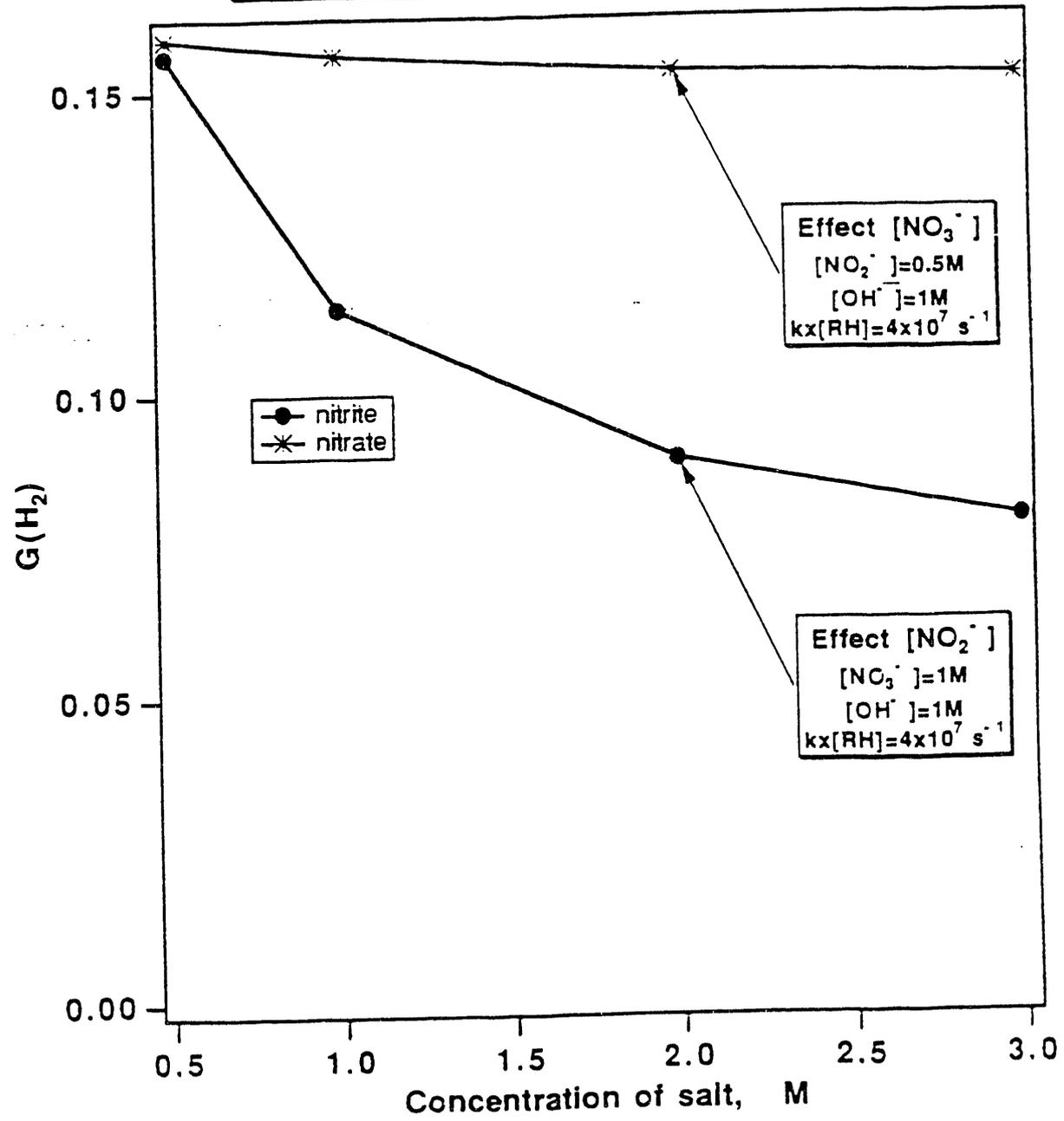
Schematic Presentation of H₂ Generation and Important Scavenging in Tank

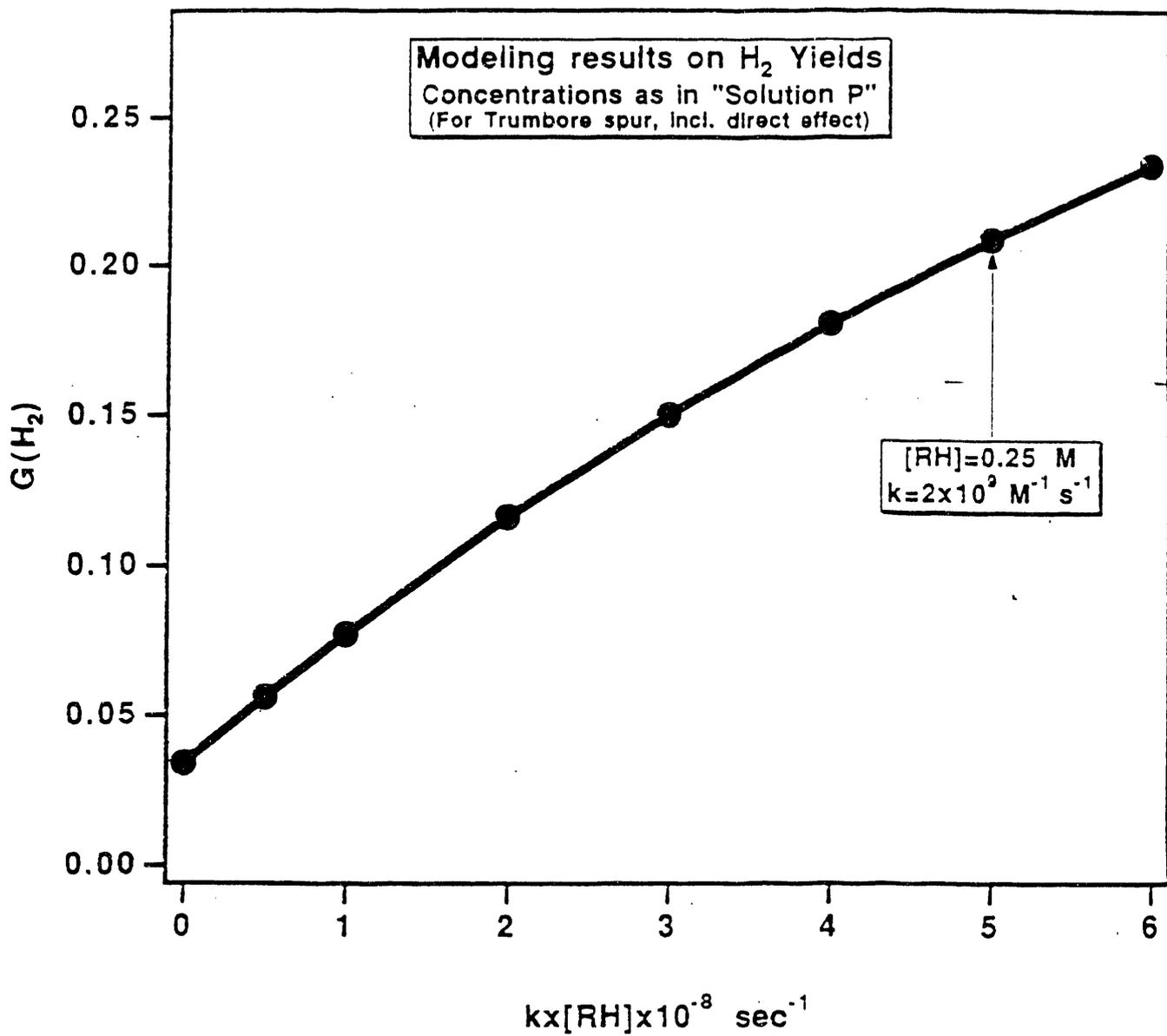


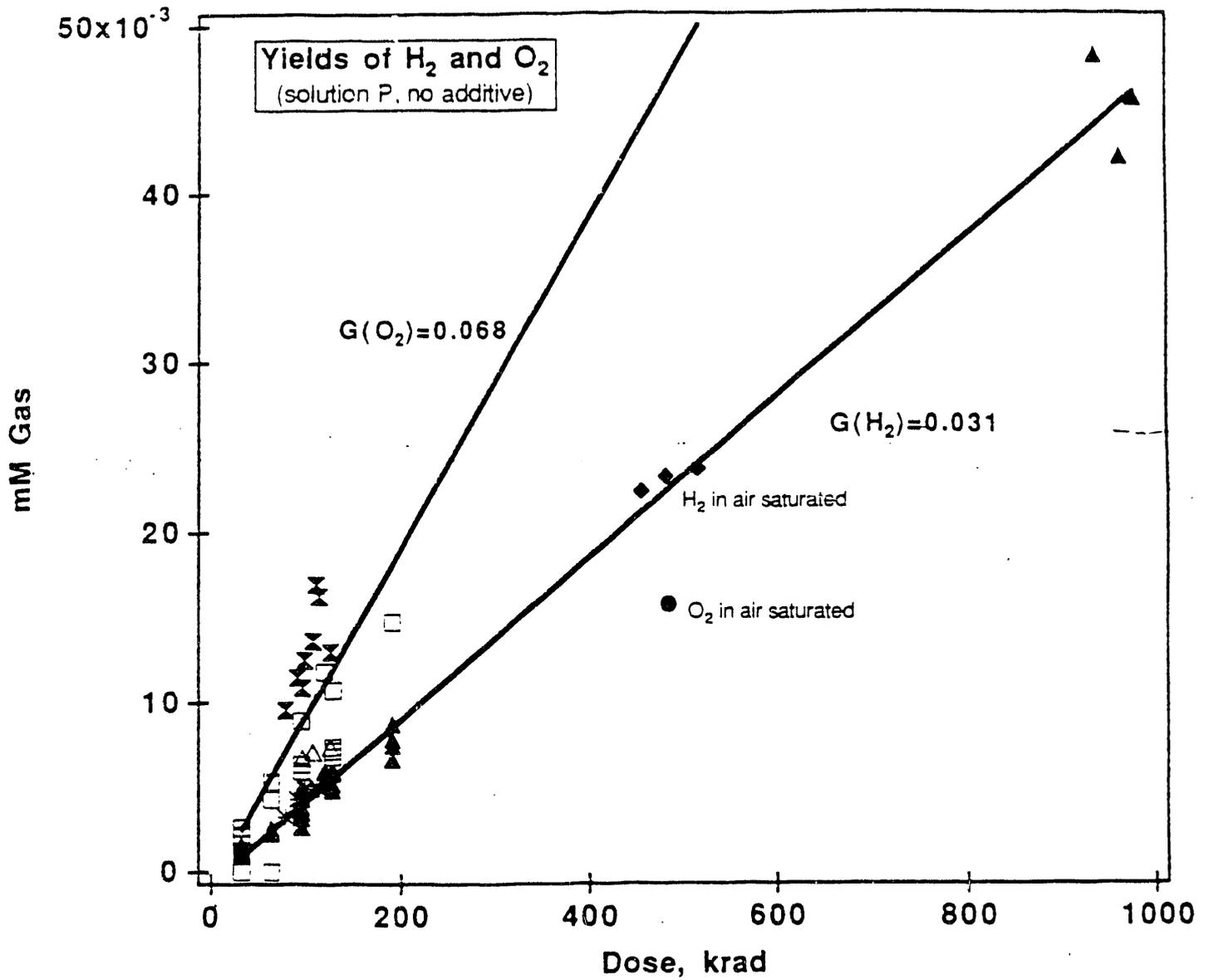




Computed Effect of NO_3^- or NO_2^- on $G(\text{H}_2)$

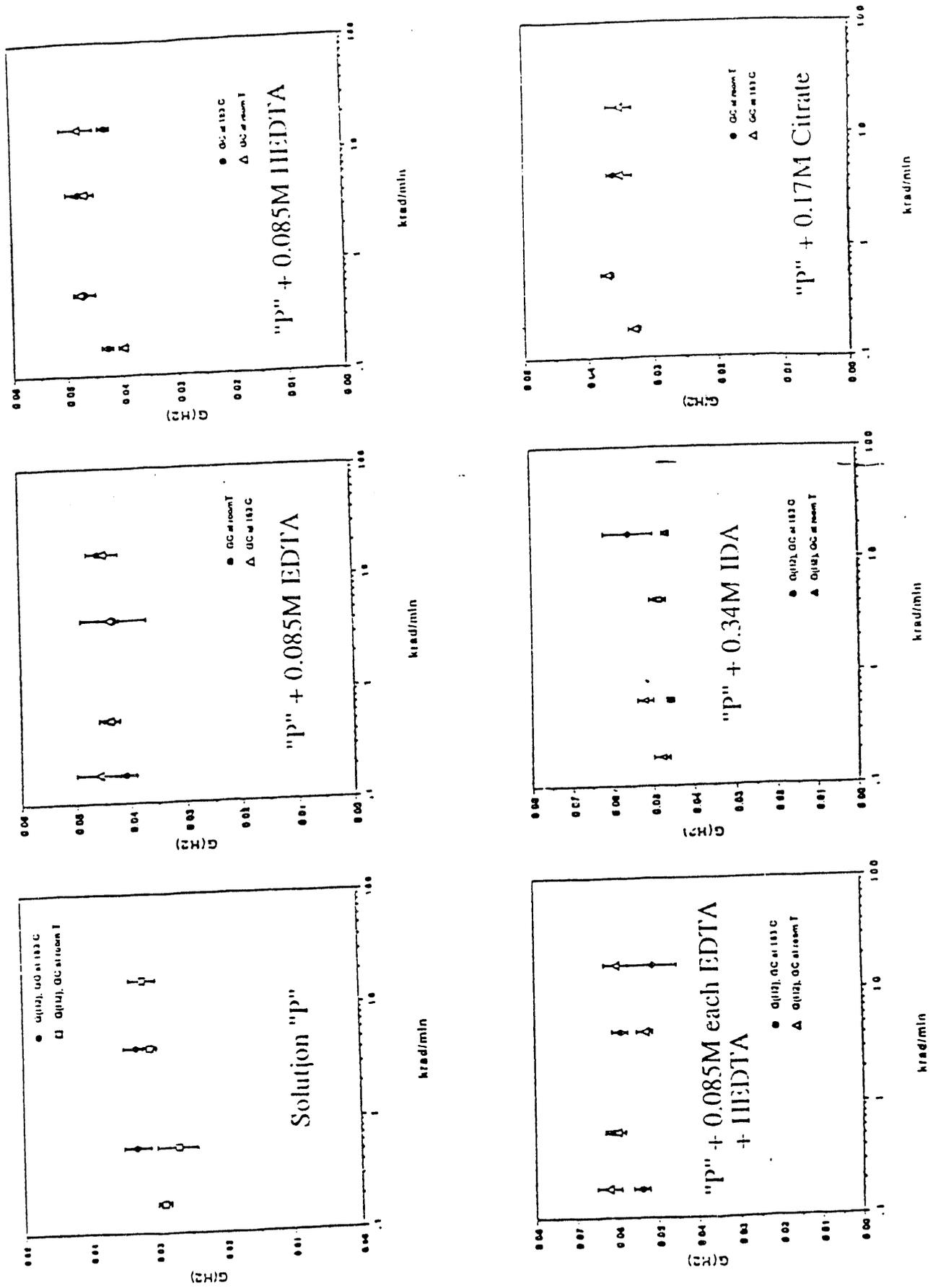




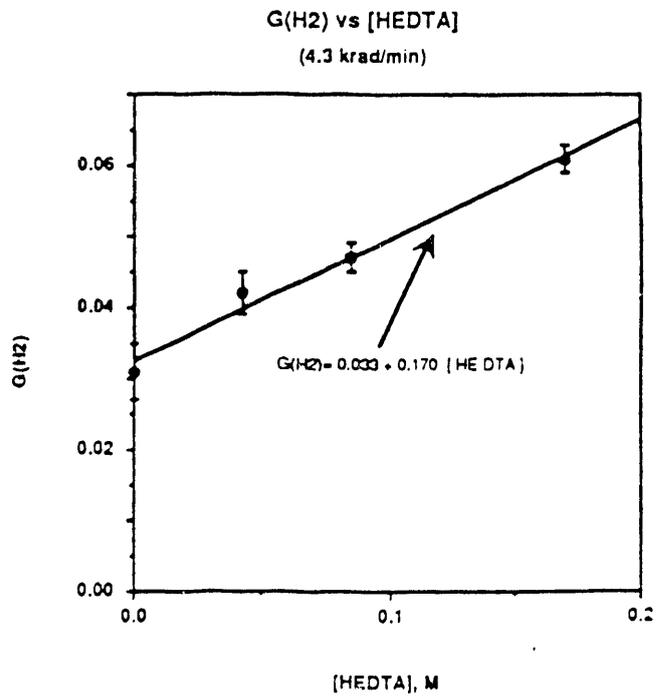
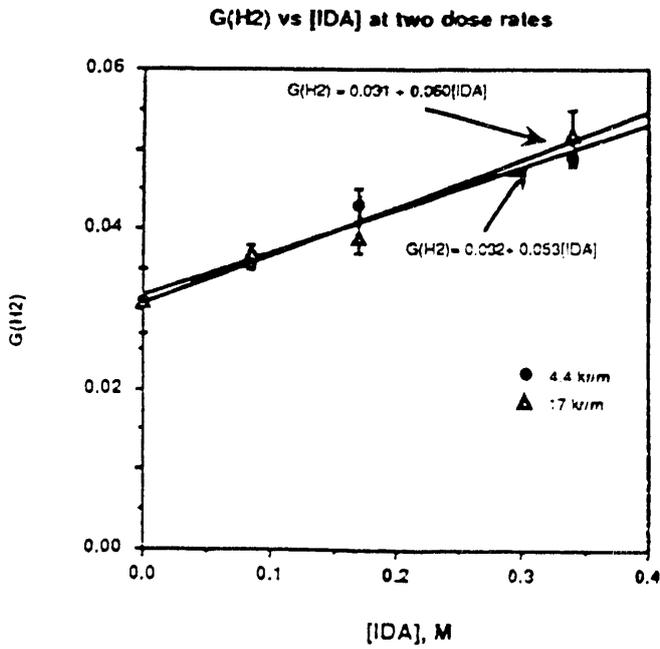
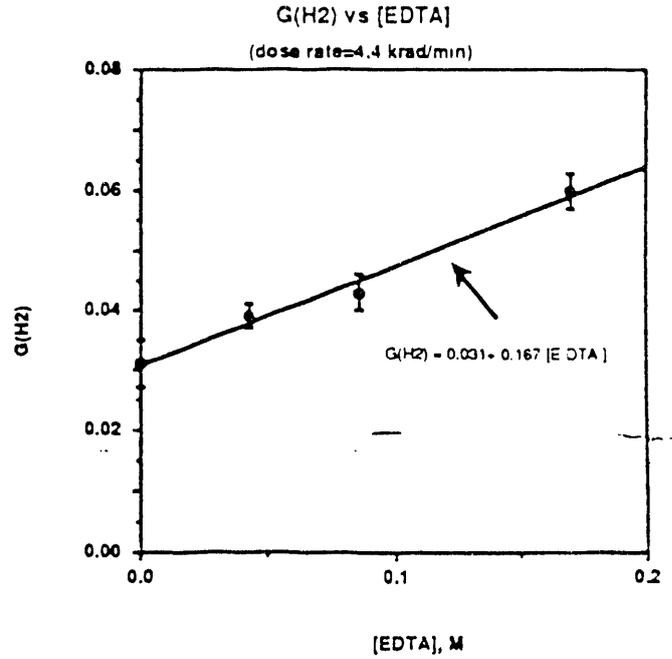
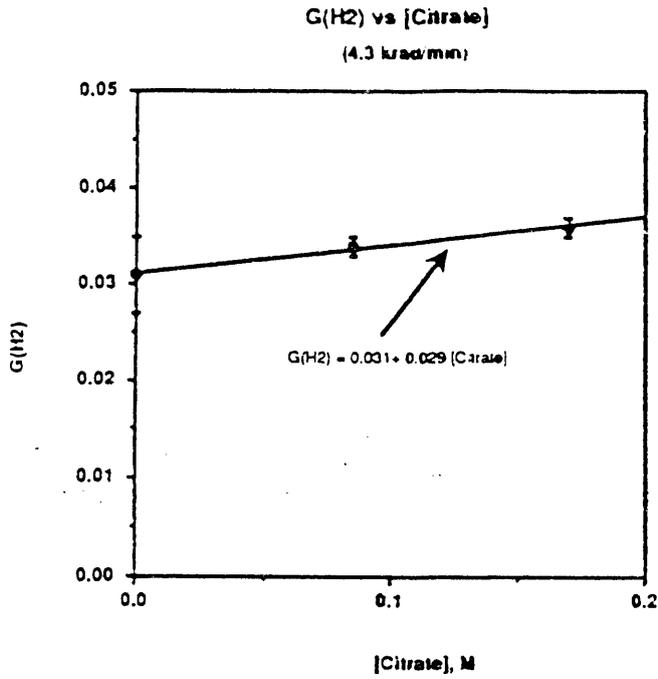


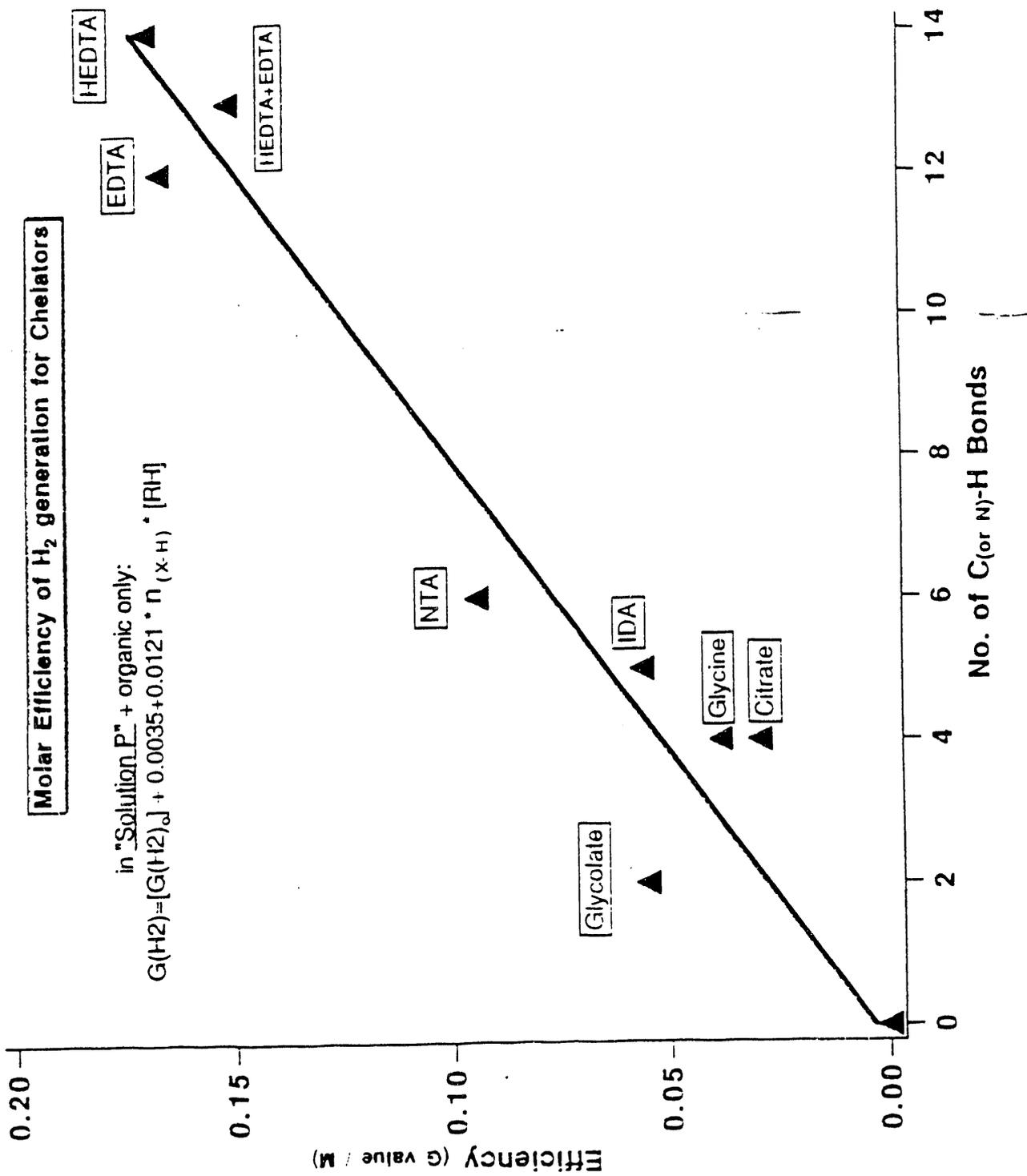
"Solution P"	{ WHC Std. }
NaOH=2.12 M	{2.00}
NaNO ₃ =2.79 M	{2.59}
NaNO ₂ =2.22 M	{2.24}
NaAlO ₂ =1.30 M	{1.54 Al(OH) ₄ }
Na ₂ CO ₃ = 0	{0.42}

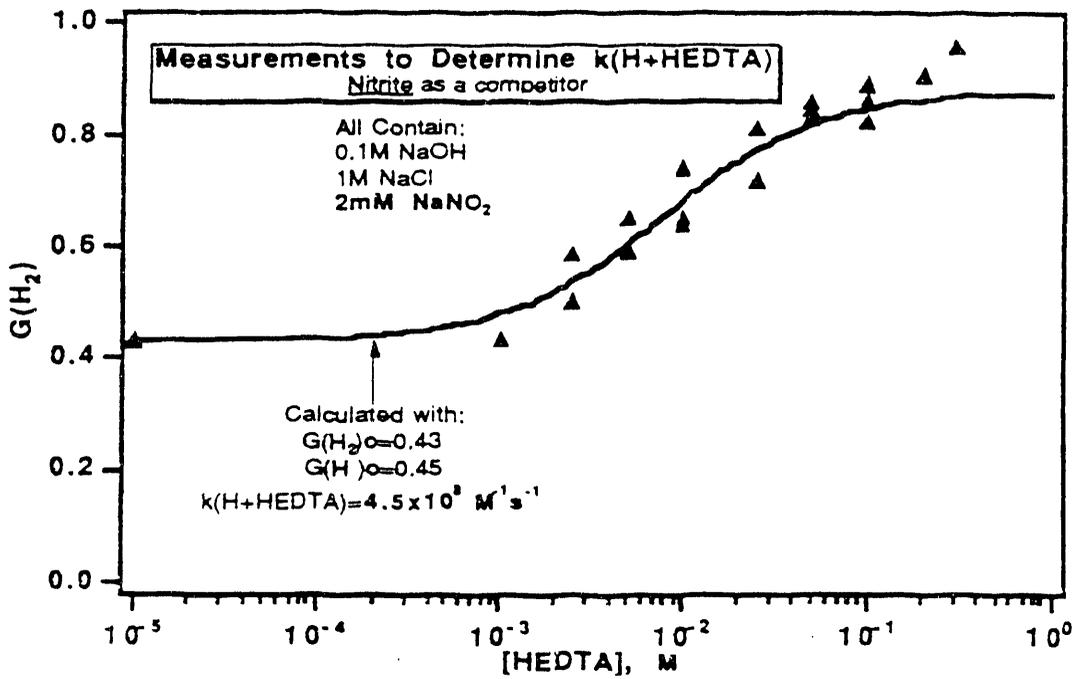
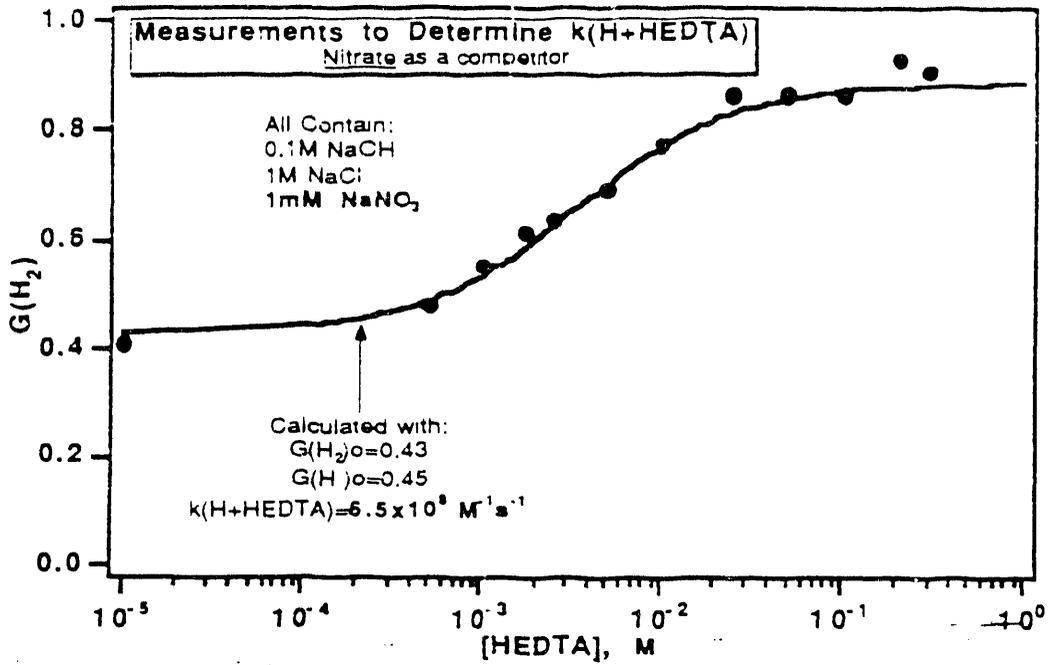
Effect of Radiation Intensity on G(H₂)



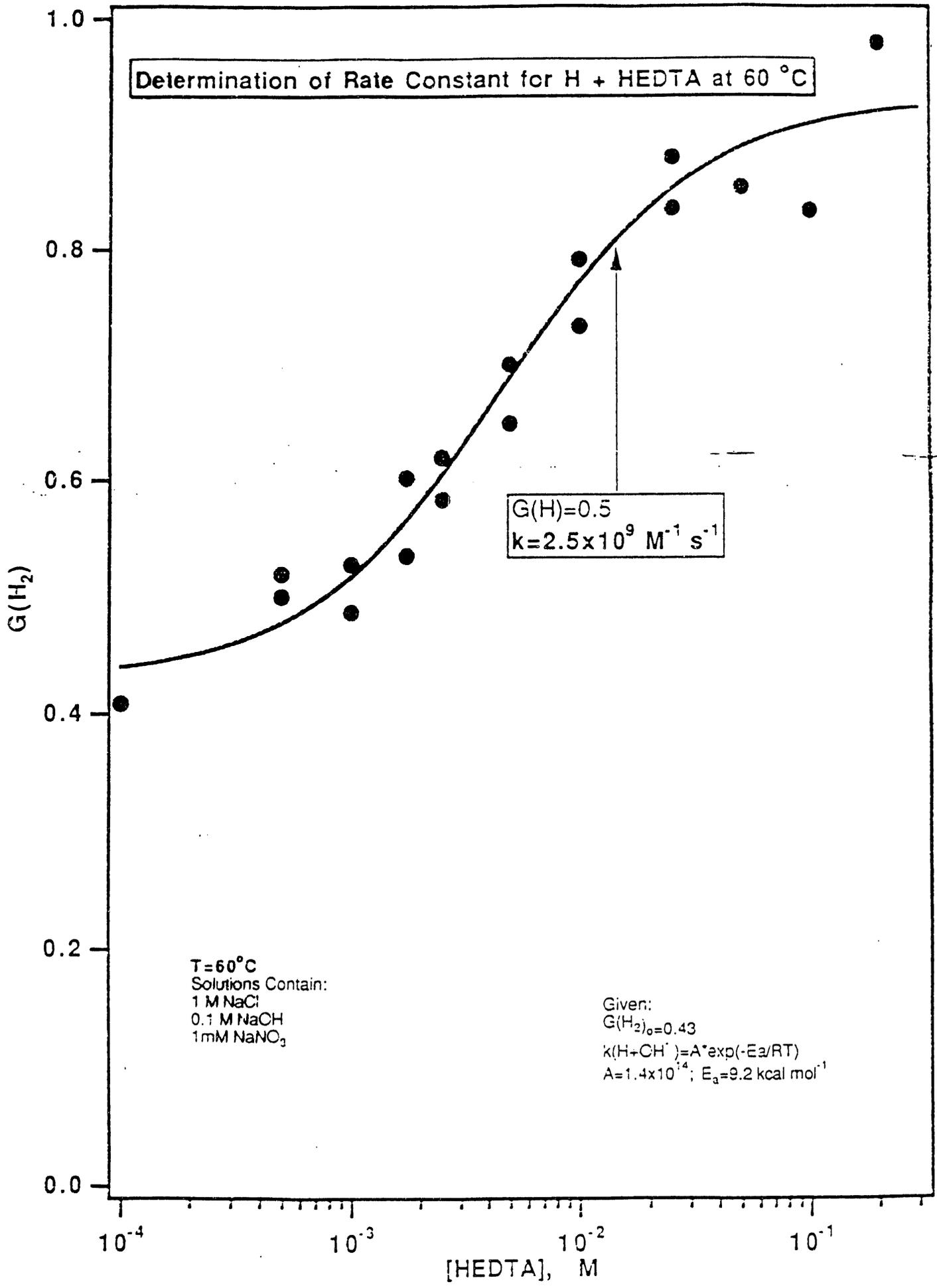
G(H₂) vs Organic Concentration







$$G(H_2) = G(H_2)_0 + G(H) \frac{k_{H+RH}[RH]}{k_{H+RH}[RH] + k_s[S]}$$

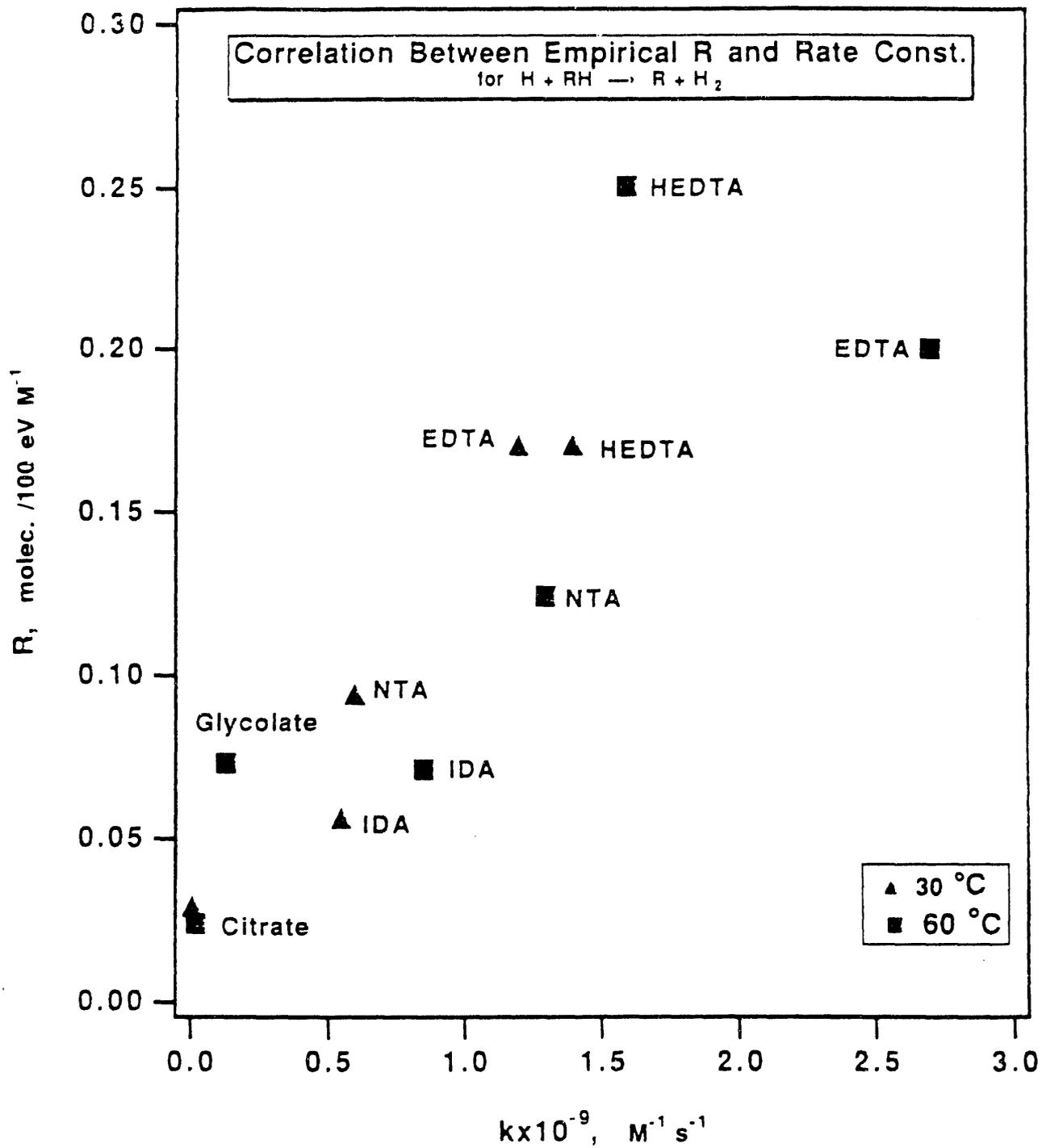


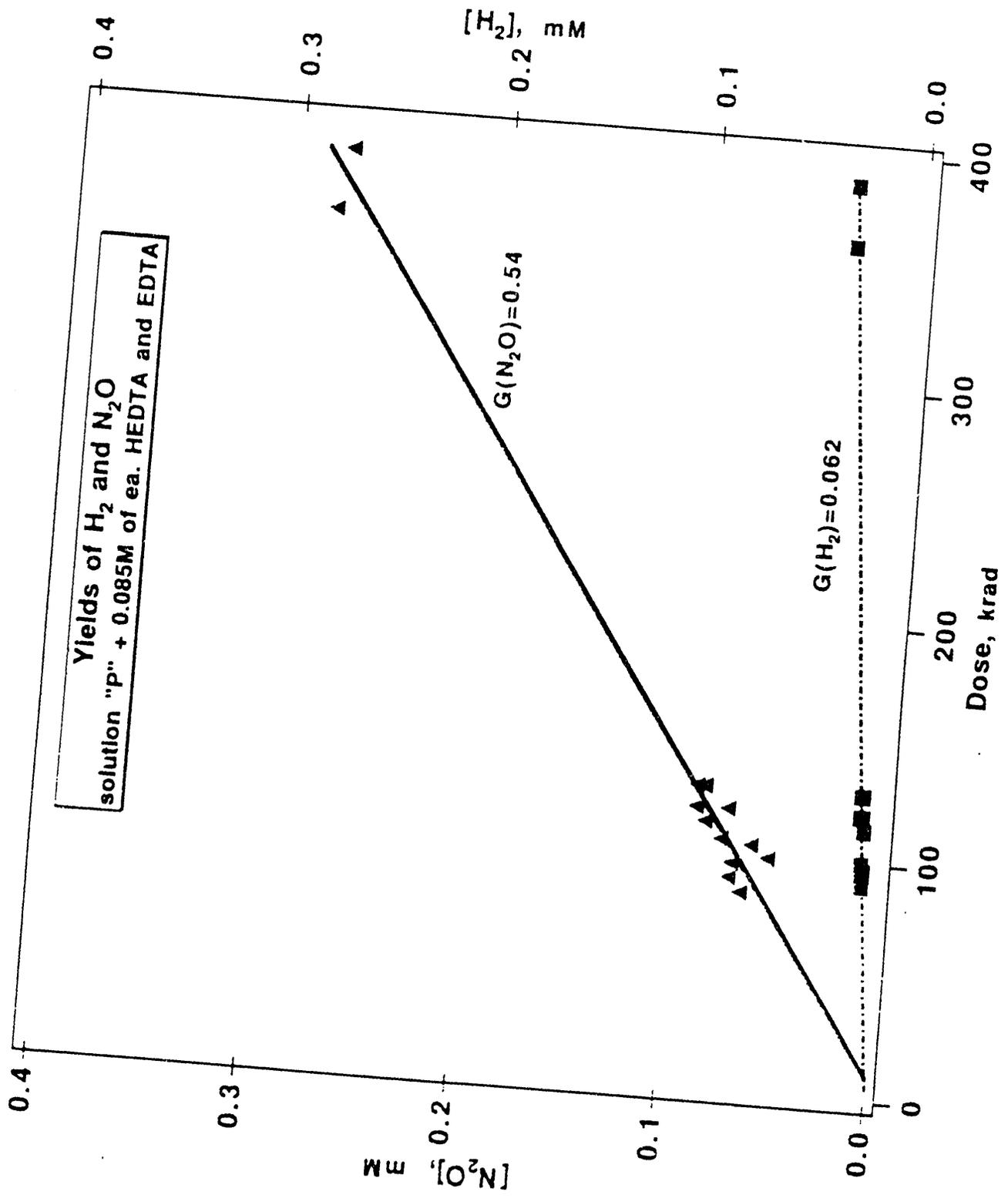
Rate Constants and Activation Parameters for the H Abstraction:



RH	$10^{-9}k_1$ at 30 °C $\text{M}^{-1} \text{s}^{-1}$	$10^{-9}k_1$ at 60 °C $\text{M}^{-1} \text{s}^{-1}$	Ea kcal M^{-1}	$10^{-9}k_1$ at 25 °C at pH 1 (literature)
EDTA	1.2	2.7	5.4	0.065
HEDTA	1.4	1.6	0.9	---
NTA	0.6	1.3	5.2	0.0075
IDA	0.55	0.85	2.9	0.00040
Glycolate		0.14		
Citrate	≈ 0.007	≈ 0.02	7.1	0.00043
OH^{a}	0.033	0.13	9.2	

^a All reaction rate constants in the table were measured against these literature values of k_2 .





Average $G(N_2O)$ for solution "P" + organics
(Irradiations at 30 °C)

Additive	Dose krad	Dose rate krad/mi n	[RH] 0.0425 M	[RH] 0.085 M	[RH] 0.17 M	[RH] 0.34 M
Glycolate	120	4.4				0.42 (at 0.3 M)
Citrate	120	4.4		not detected	0.045	
Glycine	120	4.4		0.04		0.15
	500	4.4		(at 0.1 M)		0.75 (at 0.3 M)
IDA at the Plateau)	80	17				
	120	4.4			0.75	0.68
	478	4.4			0.79	
NTA	120	4.4			0.56	
EDTA	80	17		0.40		
	121	4.4	0.63	0.59	0.50	
	370	4.4		0.32		
	500	4.4		0.75		
	94	0.55		0.33		
	167	0.18		1.04		
HEDTA	80	17		0.23		
	120	4.4	0.48	0.50	0.29 (?)	
	94	0.55		0.73		
	167	0.18		1.09		
EDTA+ HEDTA	90	17		0.33		
	120	4.4	0.7	0.60	0.50	
	360	4.4		0.55		
	96	0.55		0.91		
	160	0.18		1.18		

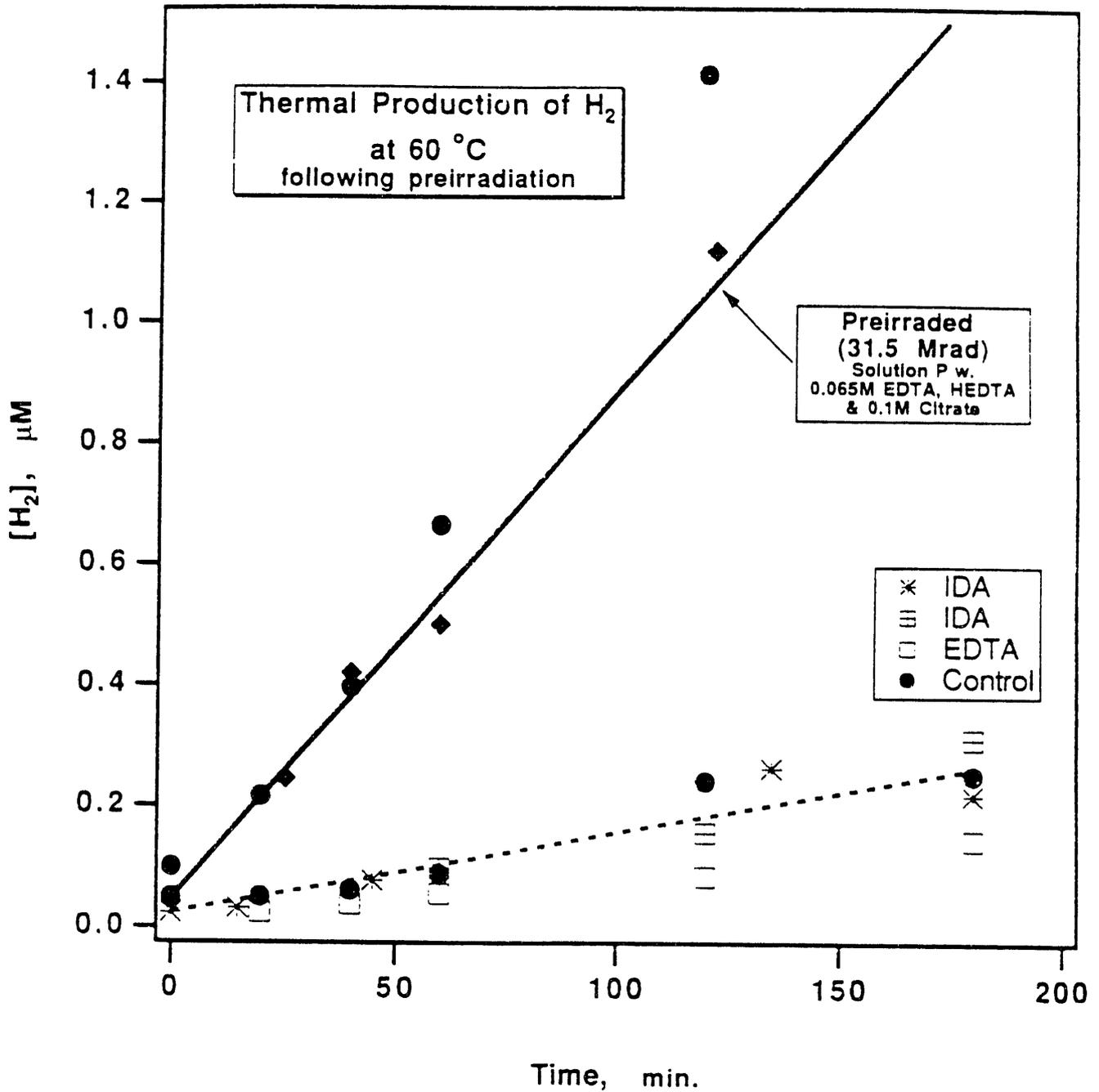
**G(H₂) and G(N₂O) at 30 and 60 °C
(incl. Preirradiation)**

Additive ^a	G(H ₂)			G(N ₂ O) ^b		
	R 30 °C (G(H ₂)/M)	R 60 °C (G(H ₂)/M)	Ratio R ₆₀ R ₃₀	G 60 °C	G 30 °C	Ratio G ₆₀ G ₃₀
None	----	----	1.06 ^c	0	0	-----
EDTA	0.167	0.341	2.04	1.10	0.60	1.80
HEDTA	0.170	0.247	1.45	0.77	0.50	1.43
NTA	0.094	0.124	1.31	0.48	0.56	0.86
IDA	0.056	0.071	1.26	0.94	0.76	1.24
Citrate	0.029	0.024	0.81	0.064	0.045	1.42
Glycine	0.038	0.040	1.05	0.47	0.15	3.10
Glycolate	0.055	0.073	1.33	0.36	0.42	2.00
POC ^b	----	----	1.40 ^c	0.37	0.49	1.30
POI ^b	----	----	1.70 ^c	1.06	0.48	2.20

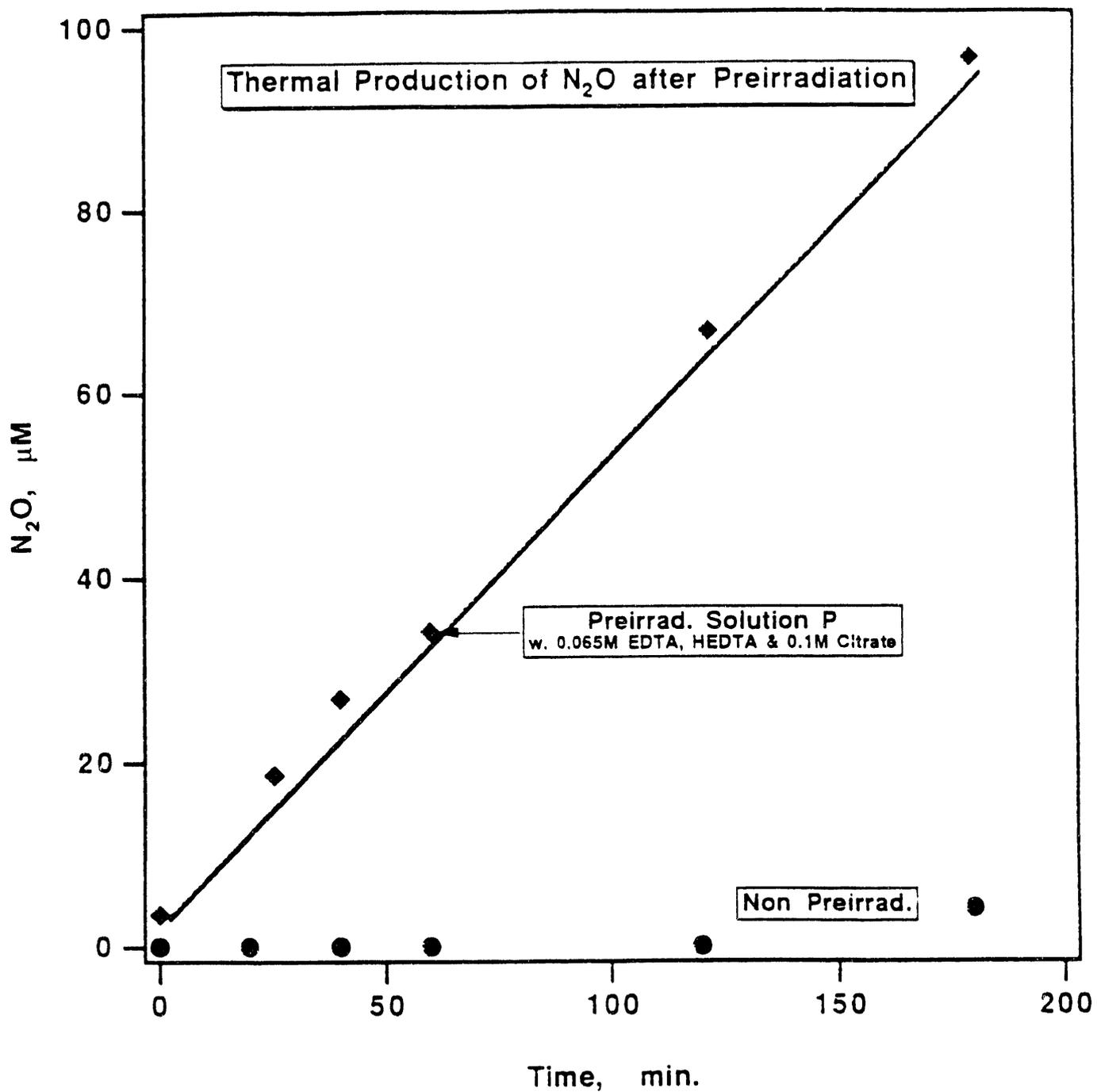
^a All samples contained solution P = 2.12 M NaOH, 1.30 M NaAlO₂, 2.22 M NaNO₂, and 2.79 M NaNO₃

^b G-values on irradiation with 130 krad at 4.4 krad/min. 0.085 M of additive.

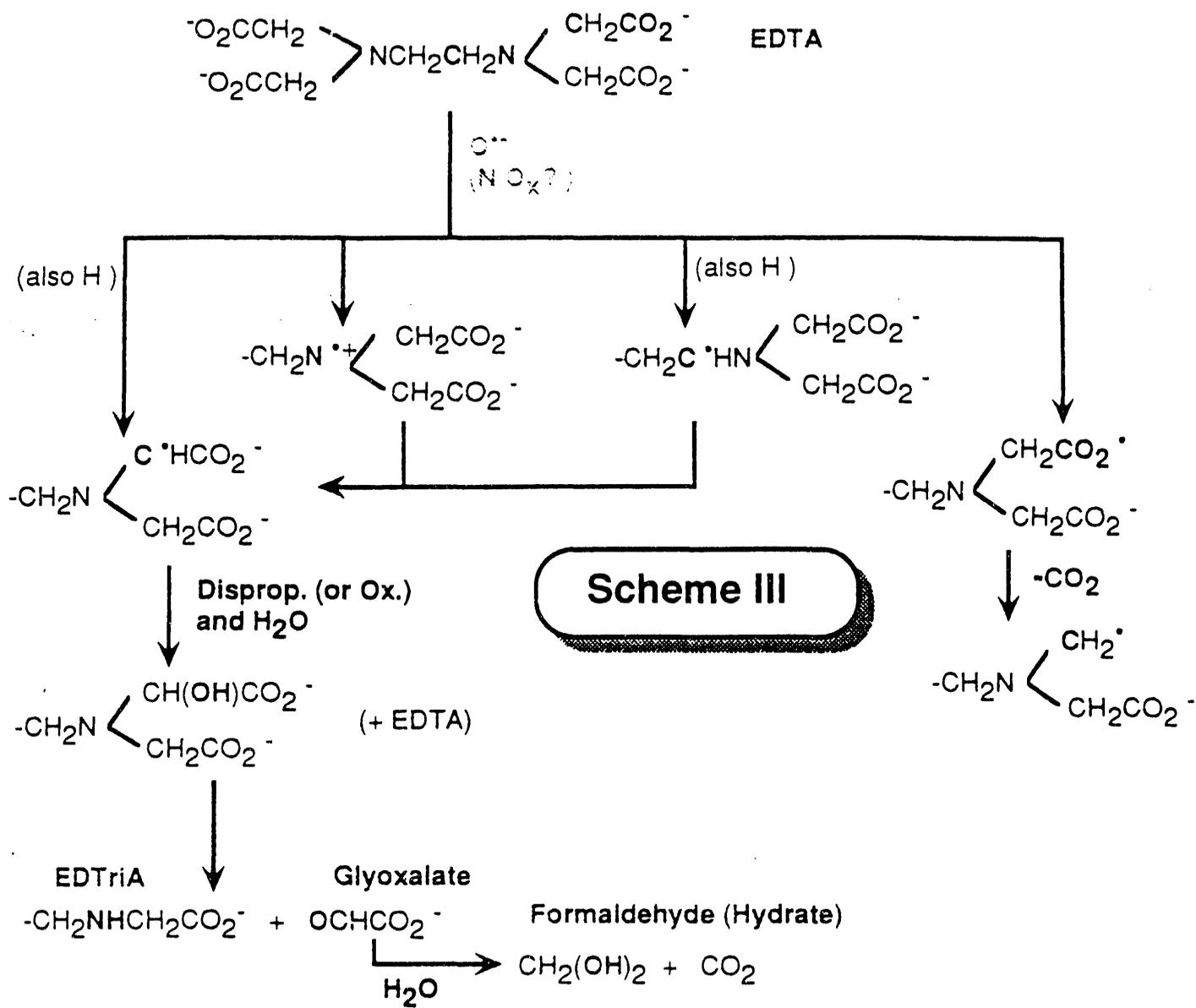
^c POI and POC contain: P+ 0.065 M of each EDTA and HEDTA, and 0.1 M citrate. Preirradiated with 31.5 Mrad at 0.51 krad/min (-2.3 years in tank). Control not preirradiated but otherwise identical.

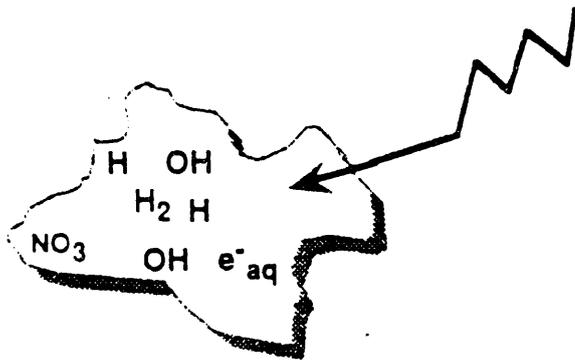
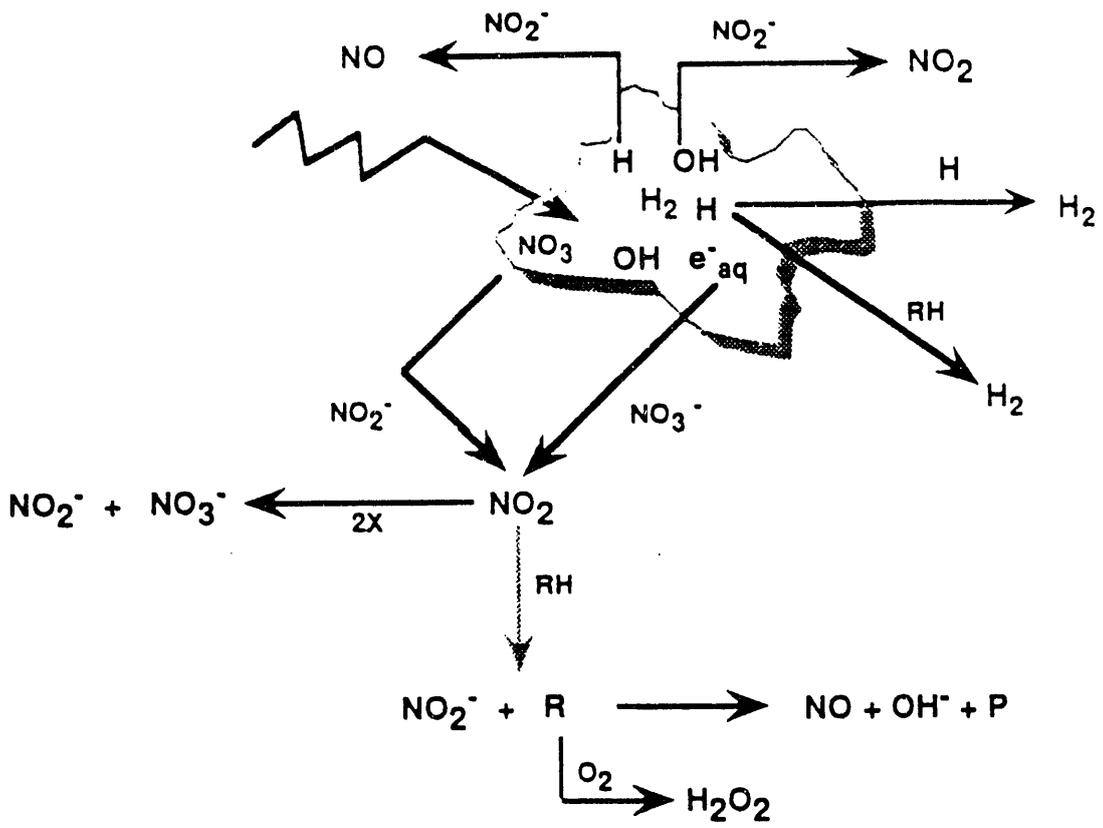


Preirradiation is equivalent to 2.5 years in 101-SY



Preirradiation was equivalent to 2.5 years in 101-SY





SUMMARY (FY 91)

1. Critical Literature Analysis:

√ Complete.

2. Modeling:

√ For G(H₂):

- * Code for non-homogeneous diffusion model has been developed and implemented to include any reaction at any concentration.
- * Sensitivity to model parameters tested - Minimal.
- * Effects of additives where tested.
- * Observations:

Yield of H₂ will be linear with $k^*[RH]$ at low k_c .

[NO₃⁻] at the level of >0.5M is inconsequential.

Sensitive to [NO₂⁻].

If [NO₂⁻] > 2.0 M no scavenger (incl. NO₂⁻) will be effective.

√ For G(H₂O₂):

- * Same code and model was used.
- * More sensitive to model parameters than G(H₂).
- * Yields are similar to G(H₂).
- * Strongly depends on [NO₂⁻] and on $k_{OH^+}[RH]$ (weakly on NO₃⁻). Increasing either one will decrease G(H₂O₂).

√ For NO_x system:

- * Code for homogeneous kinetics developed.
- * Tested without organic - No N₂O produced.

No information on organic — NO_x.

3. Experimental:

√ Room Temperature :

- * $G(\text{H}_2)$ and $G(\text{O}_2)$ were determined in simulated waste
No N_2O or N_2 detected when no RH.
- * O_2 is consumed ($G(-\text{O}_2)=7.0$) when RH is present.
- * $G(\text{H}_2)$ increases linearly with [RH].
- * Two Mechanisms for Radiolytic H_2 Production were verified.
- * High N_2O yields are obtained in the presence of the organic.
Inversely dose-rate dependent; nearly independent of [RH]
but RH is required.
- * Source of nitrogen in N_2O is not organic

√ Elevated Temperature :

- * $G(\text{H}_2)$ and $G(\text{N}_2\text{O})$ increase with temperature.
- * N_2 is observed in some cases.

√ Preirradiation :

- * Small effect on $G(\text{H}_2)$ and $G(\text{N}_2\text{O})$.
- * Strong temperature effect.
- * Strong enhancement of thermal generation of H_2 and N_2O .

Future :

- * Radiolysis of Heterogeneous Systems.
- * NH_3 Yields and $\text{H}_2/\text{N}_2\text{O}$ Ratio.
- * Gas Retention.

Appendix H

Mechanistic Elucidation of Chemistry in Tank 101-SY

Mechanistic Elucidation of Chemistry in Tank 101-SY

Tank Waste Science Panel Meeting

Hanford, Washington

November 11-13, 1991

Professors: E.C. Ashby
E. Kent Barefield
Charles L. Liotta
Henry M. Neumann

Post Doctoral Assistants:

Fabio Doctorovich
Ashok Konda
Kai Zhang

M.S. Chemist: Jeff Hurley

Technicians: D. Allen Annis
M. Juliao

PROPOSED MECHANISM OF THERMAL DEGRADATION OF GLYCOLATE

- 1) $\text{Al}(\text{OH})_4^- + \text{NO}_2^- \rightleftharpoons \text{Al}(\text{OH})_3\text{-O-N=O}^- + \text{OH}^-$
- 2) $\text{Al}(\text{OH})_3\text{-O-N=O}^- + \text{HO-CH}_2\text{-CO}_2^- \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{O=N-O-CH}_2\text{-CO}_2^-$
- 3) $\text{O=N-O-CH}_2\text{-CO}_2^- \rightarrow \text{NO}^- + \text{O=CH}_2 + \text{CO}_2$
- 4) $\text{O=N-O-CH}_2\text{-CO}_2^- + \text{OH}^- \rightarrow \text{NO}^- + \text{H-(CO)-CO}_2^- + \text{H}_2\text{O}$
- 5) $2\text{NO}^- \rightleftharpoons \text{N}_2\text{O}_2^{2-}$
- 6) $\text{N}_2\text{O}_2^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HN}_2\text{O}_2^- + \text{OH}^-$
- 7) $\text{HN}_2\text{O}_2^- \rightarrow \text{N}_2\text{O} + \text{OH}^-$
- 8) $\text{N}_2\text{O} + \text{Al}(\text{OH})_3\text{-O-N=O}^- \rightarrow \text{N}_2 + \text{Al}(\text{OH})_3\text{-O-N=O}$
- 9) $\text{N}_2\text{O} + \text{NO}_2^- \rightarrow \text{N}_2 + \text{NO}_3^-$
- 10) $\text{CH}_2=\text{O} + \text{OH}^- \rightleftharpoons \text{HO-CH}_2\text{-O}^-$
- 11) $\text{HO-CH}_2\text{-O}^- + \text{OH}^- \rightleftharpoons \text{O-CH}_2\text{-O}^- + \text{H}_2\text{O}$
- 12) $\text{O-CH}_2\text{-O}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H-COO}^- + \text{OH}^-$
- 13) $\text{H-(CO)-CO}_2^- + \text{OH}^- \rightleftharpoons \text{O-CH(OH)-CO}_2^- \rightleftharpoons (\text{O})_2\text{-CH-CO}_2^-$
- 14) $(\text{O})_2\text{-CH-CO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2\text{C-CO}_2^- + \text{OH}^-$

EXPERIMENTAL OBSERVATIONS CONCERNING GAS EVOLUTION

- 1) After initial gas expansion during the heating process, induction periods of 20 to 70 hours were observed.
(EXPERIMENT A34)
- 2) No gas was evolved in the absence of an organic component.
(EXPERIMENT B1)
- 3) When EDTA was the organic component no gas was evolved under air or argon atmospheres.
(EXPERIMENTS A22 AND A26)
- 4) When HEDTA was the organic component the rate of gas evolution under a helium atmosphere was ≈ 0.21 mL/hour. In an air atmosphere the rate is ≈ 0.39 mL/hour.
(EXPERIMENTS A50 AND A113)
- 5) When HEDTA was used as the organic substrate stirring of the reaction mixture had no effect on the induction period.

- 6) Using HEDTA as the organic component, the rate of gas evolution with sonication is ≈ 0.25 mL/hour. The rate in the absence of sonication is ≈ 0.39 mL/hour.
(EXPERIMENTS A97 AND A97 EXPANDED)

- 7) When glycolate was the organic component the rate of gas evolution under an air or helium atmosphere was approximately ≈ 0.34 mL/hour.
(EXPERIMENTS A119 AND A126)

- 8) When sodium aluminate was omitted from the "final word" mixture using glycolate as the organic component under an air atmosphere, no gas evolution was observed.
(EXPERIMENT A111)

- 9) When sodium nitrite was omitted from the "final word" mixture using glycolate as the organic component under an air atmosphere a minuscule amount of gas, ≈ 20 mL, was evolved over a 400 hour period.
(EXPERIMENT A78)

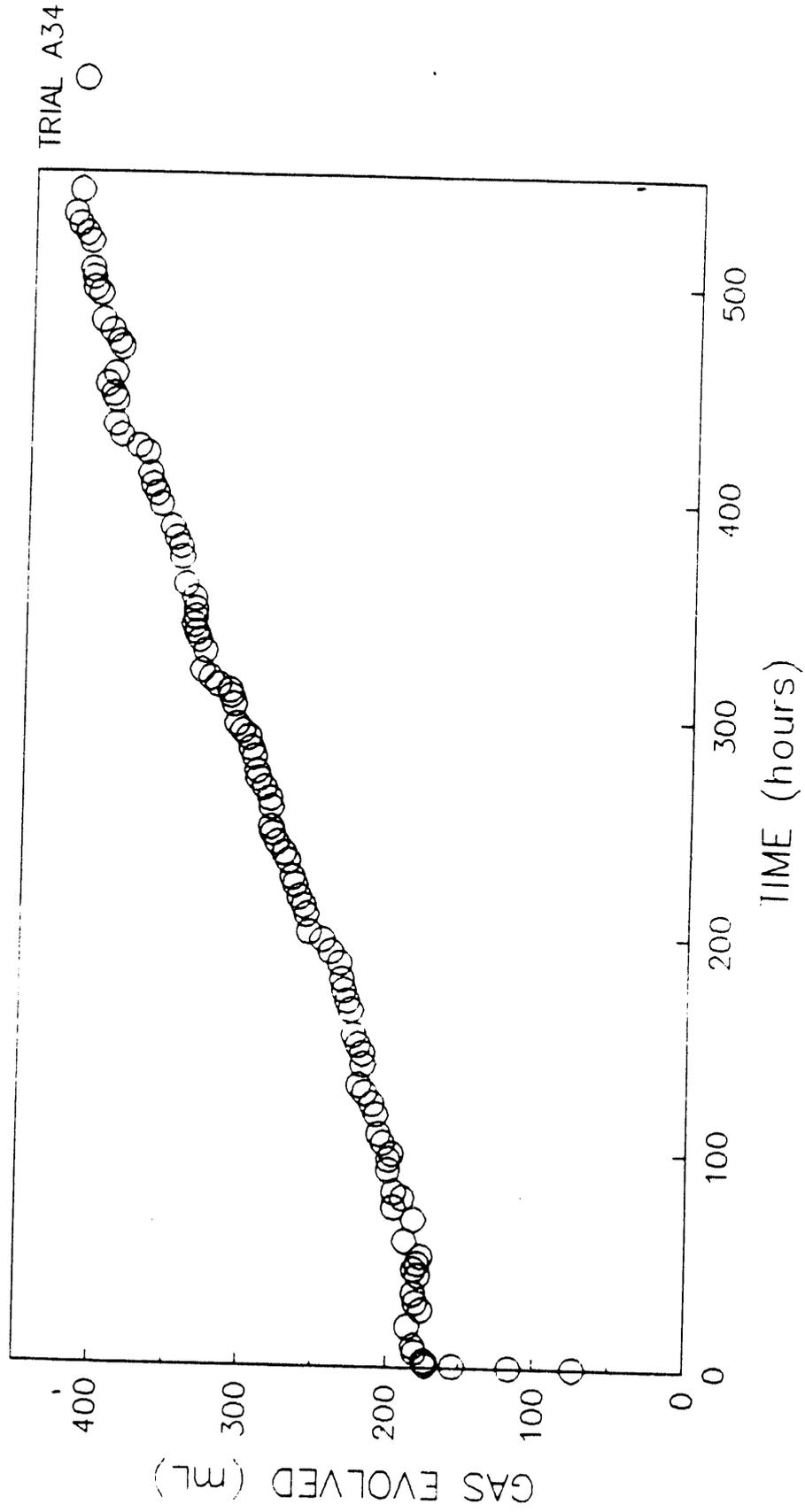
10) When sodium nitrate was omitted from the "final word" mixture using glycolate as the organic component under an air atmosphere gas was evolved at approximately 0.31 mL/hour.

(EXPERIMENT A84)

11) Experiments using glycolate as the organic component under both air and helium atmospheres in the presence of catalytic amounts of chromium (Cr^{III} and Cr^{VI}) are currently under investigation. Under a helium atmosphere the rate of gas evolution is approximately 0.50 mL/hour. Under an air atmosphere the rate of gas evolution is approximately 0.13 mL/hour.

(EXPERIMENTS B4 AND B11)

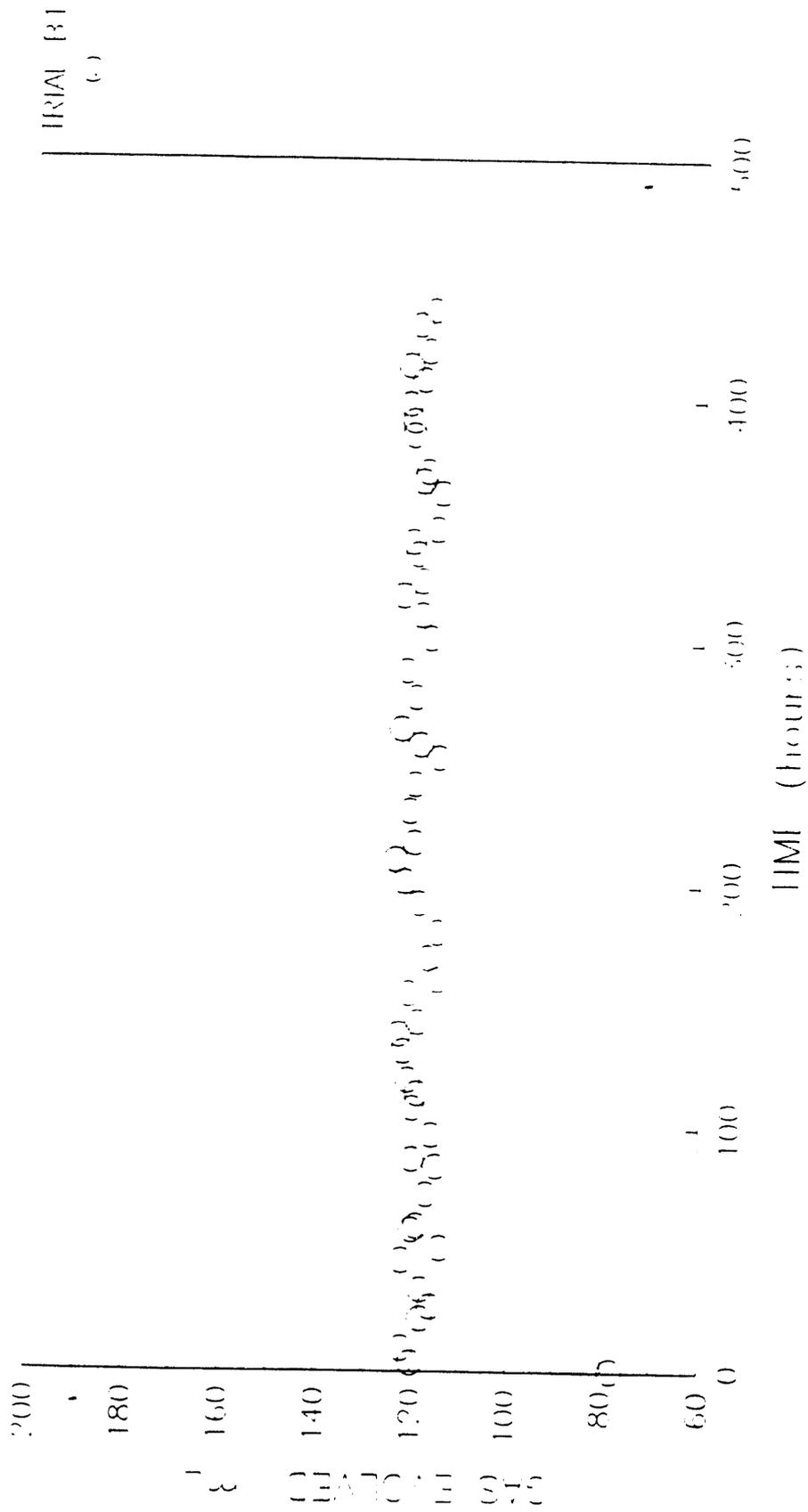
GAS EVOLUTION TRIAL A34
HOMOGENEOUS CONDITIONS
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus 5

uncorrected for temperature and pressure

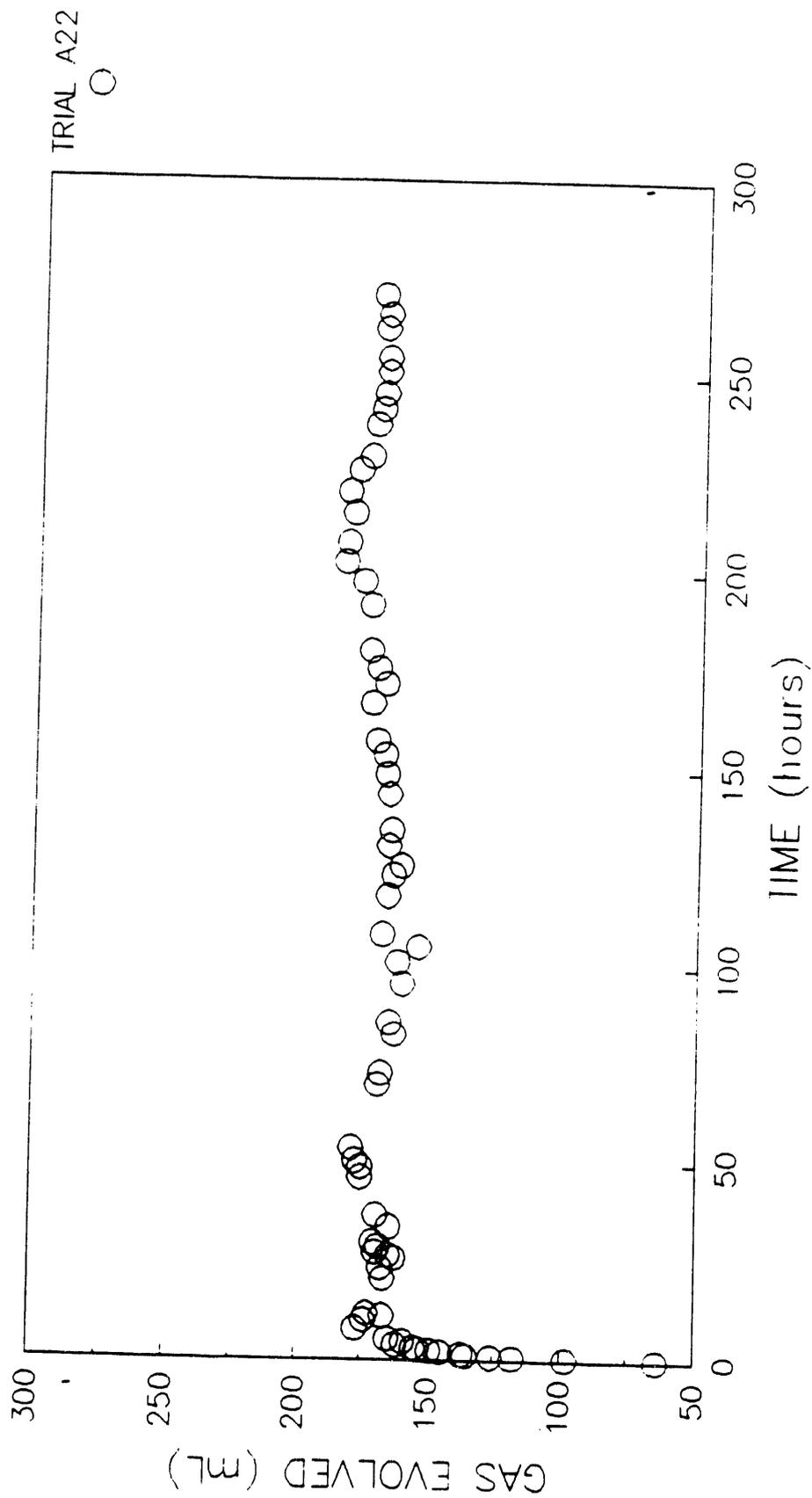
GAS EVOLUTION TRIAL B1
HOMOGENEOUS CONDITIONS
NO ORGANIC UNDER AIR ATMOSPHERE



reaction apparatus 5.

uncorrected for temperature and pressure

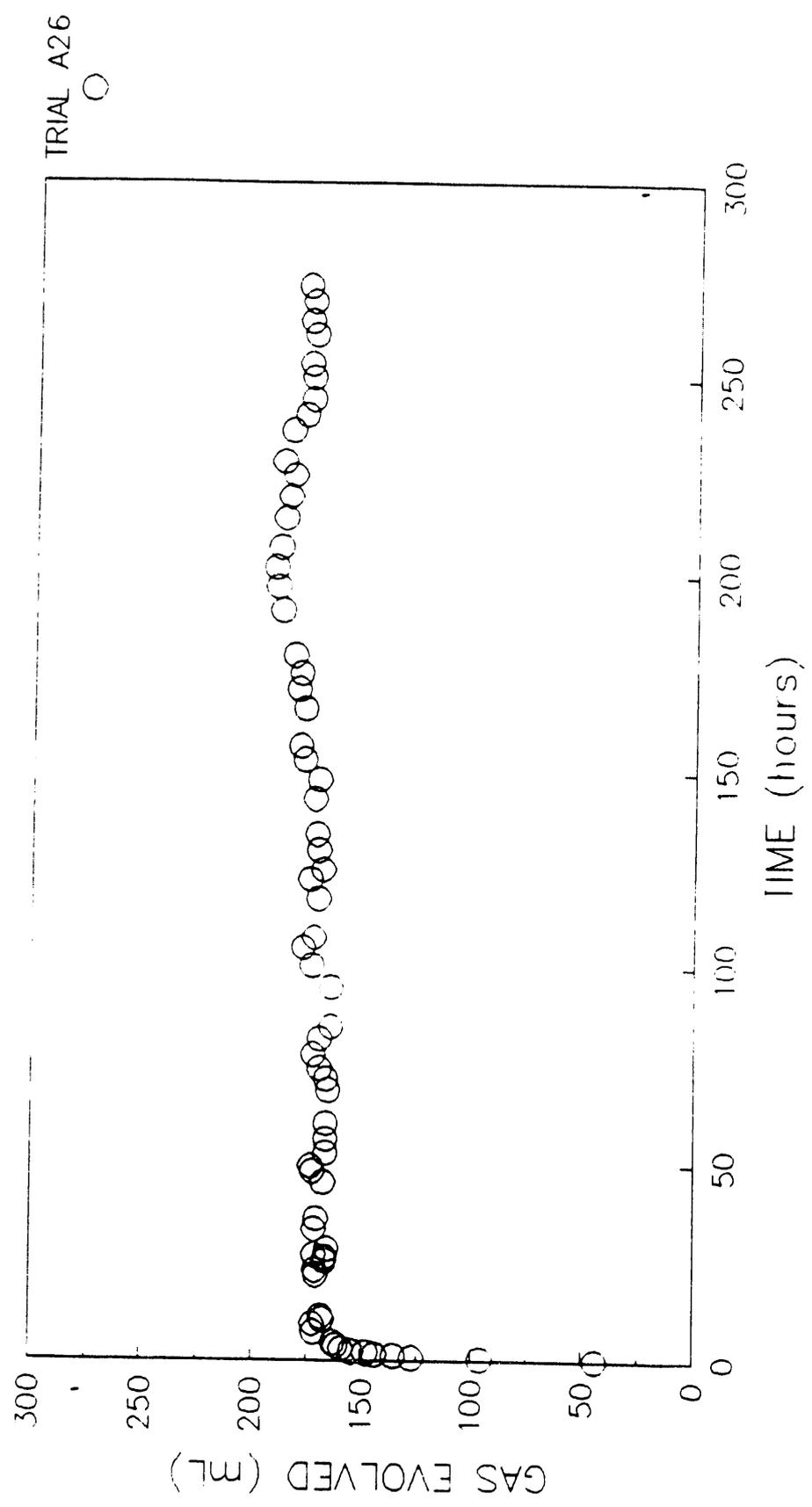
GAS EVOLUTION TRIAL A22
HOMOGENEOUS CONDITIONS
EDTA UNDER ARGON ATMOSPHERE



reaction apparatus 2

uncorrected for temperature and pressure

GAS EVOLUTION TRIAL A26
HOMOGENEOUS CONDITIONS
EDTA UNDER AIR ATMOSPHERE



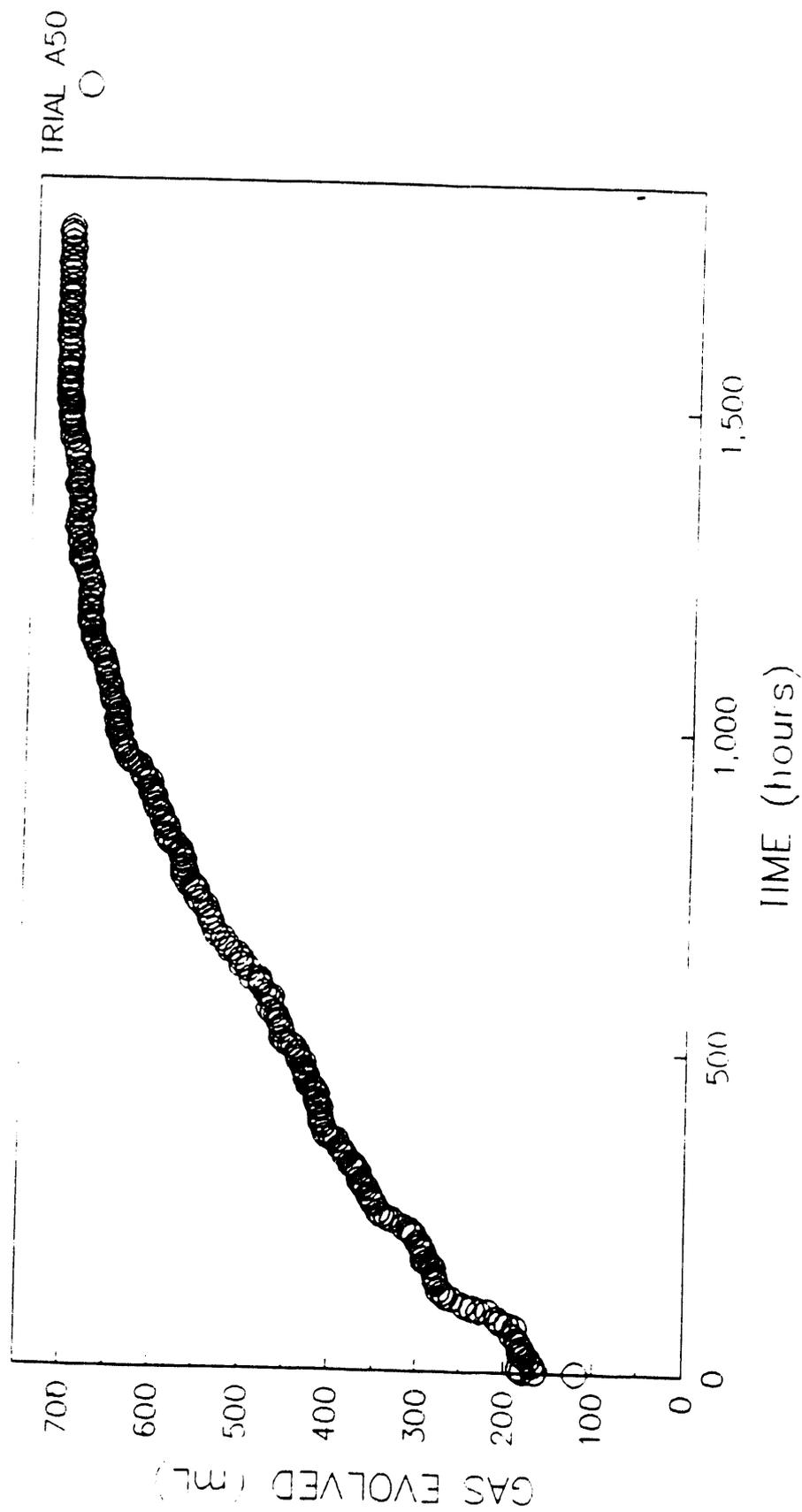
reaction apparatus 4

uncorrected for temperature and pressure

GAS EVOLUTION TRIAL A50

HOMOGENEOUS CONDITIONS

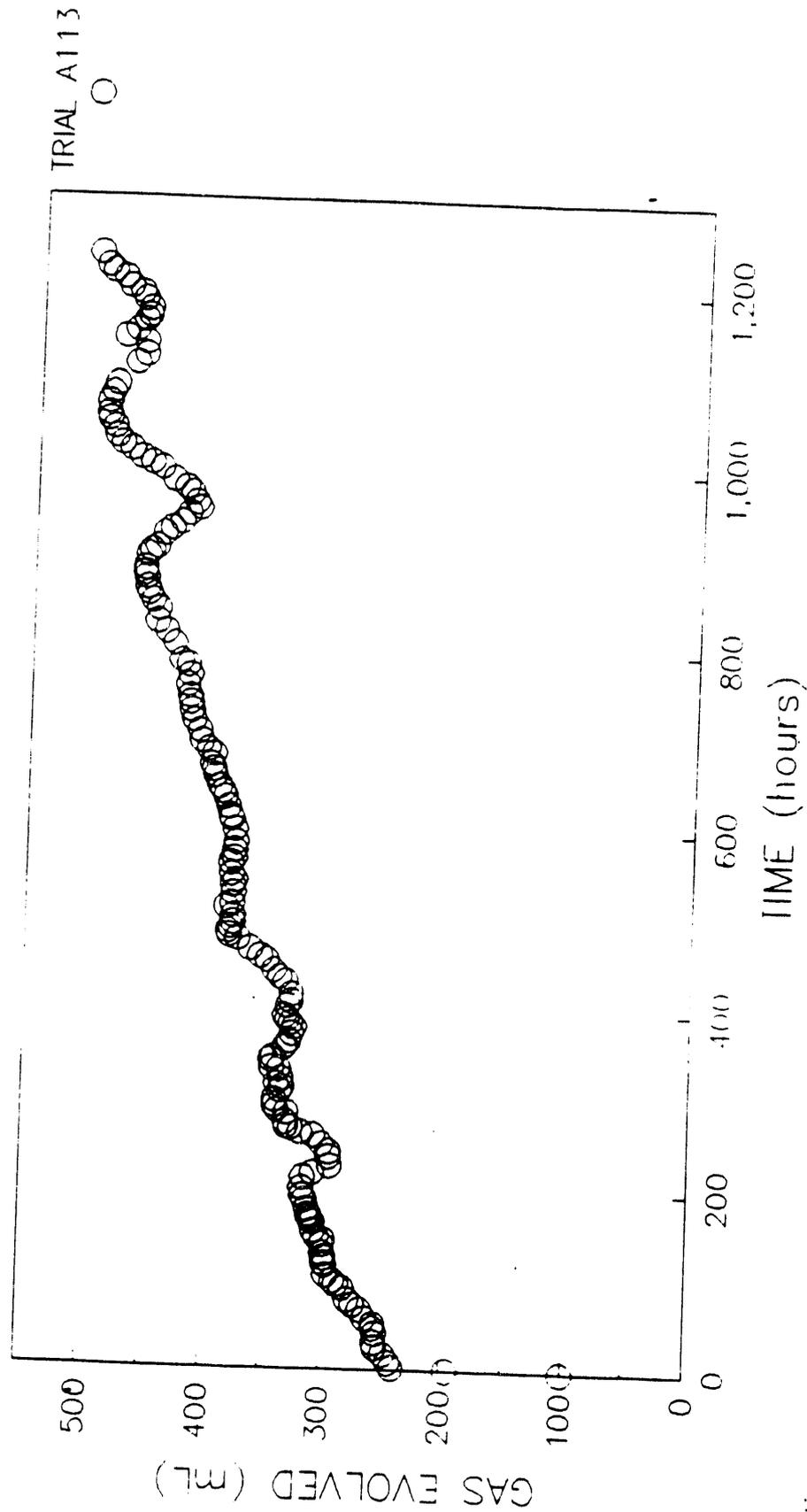
HEDTA UNDER AIR ATMOSPHERE



reaction apparatus 1

uncorrected for temperature and pressure

GAS EVOLUTION TRIAL A113
HOMOGENEOUS CONDITIONS & DEOXYGENATED WATER
HEPTA UNDER HELIUM ATMOSPHERE



reaction apparatus 5

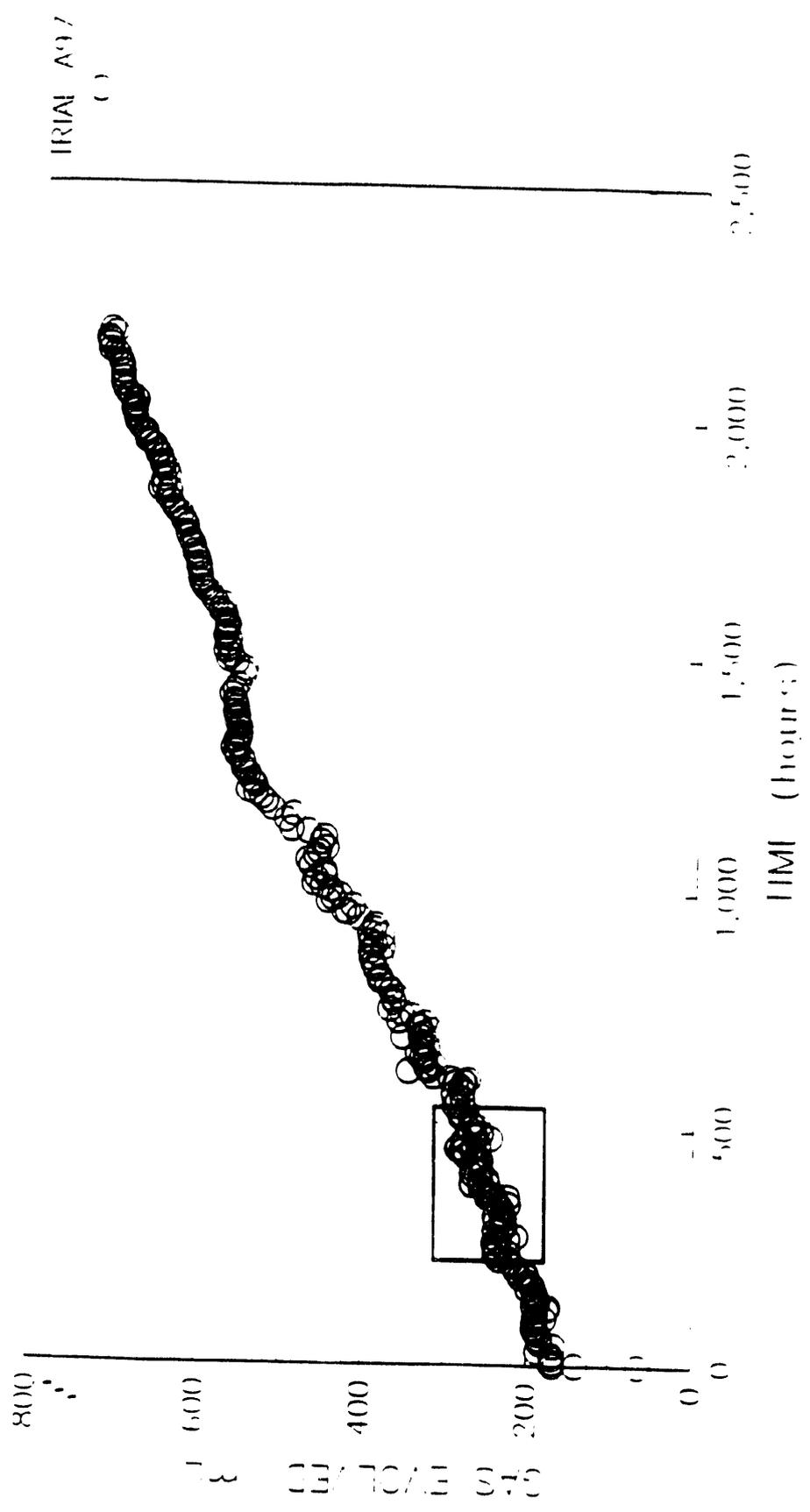
vessel popped open at 12.36 hours

uncorrected for temperature and pressure

GAS EVOLUTION TRIAL A97

HOMOGENEOUS CONDITIONS WITH SONICATION

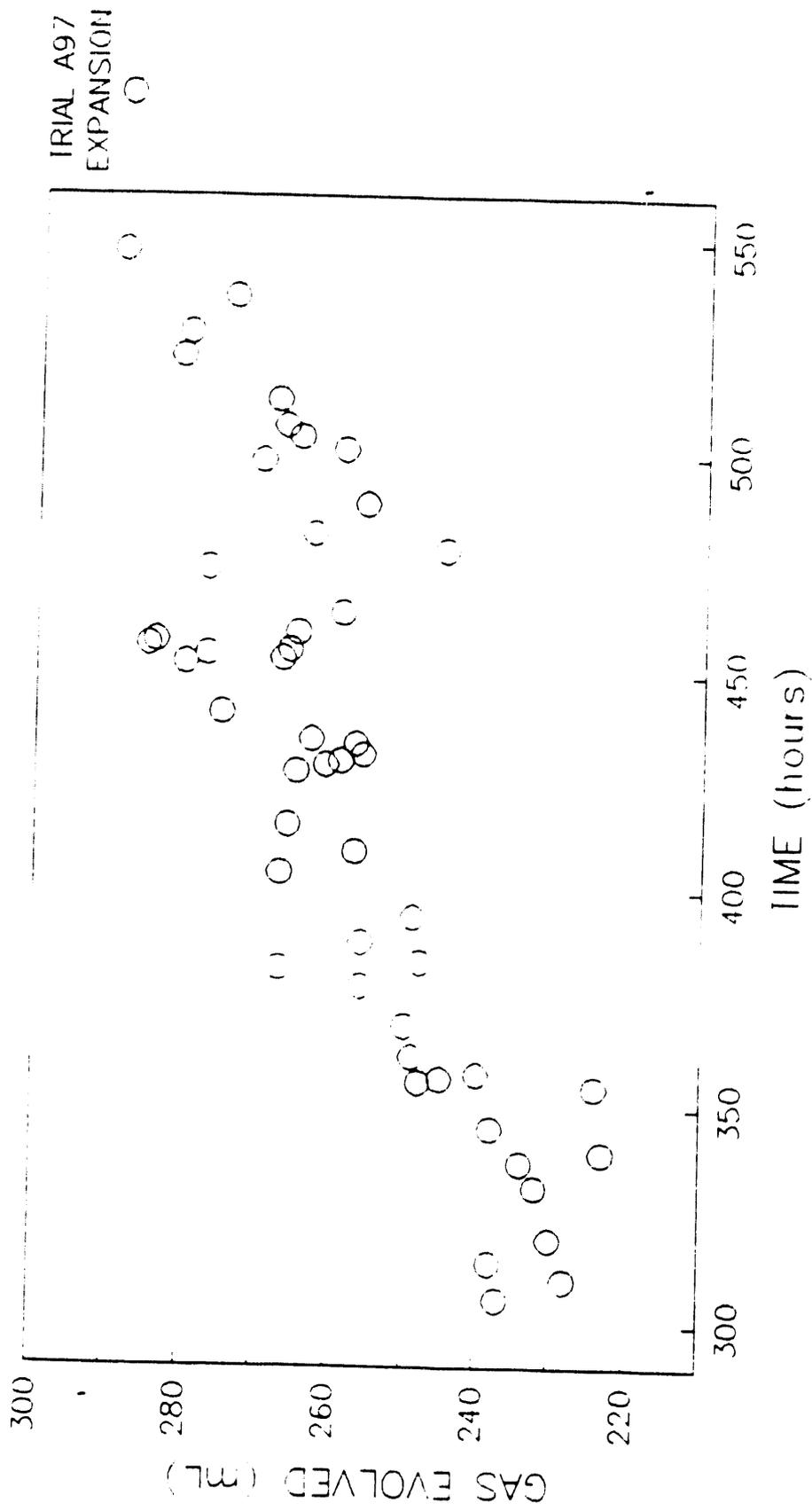
METHA UNDER AIR ATMOSPHERE



reaction apparatus 2

units are used for temperature and pressure

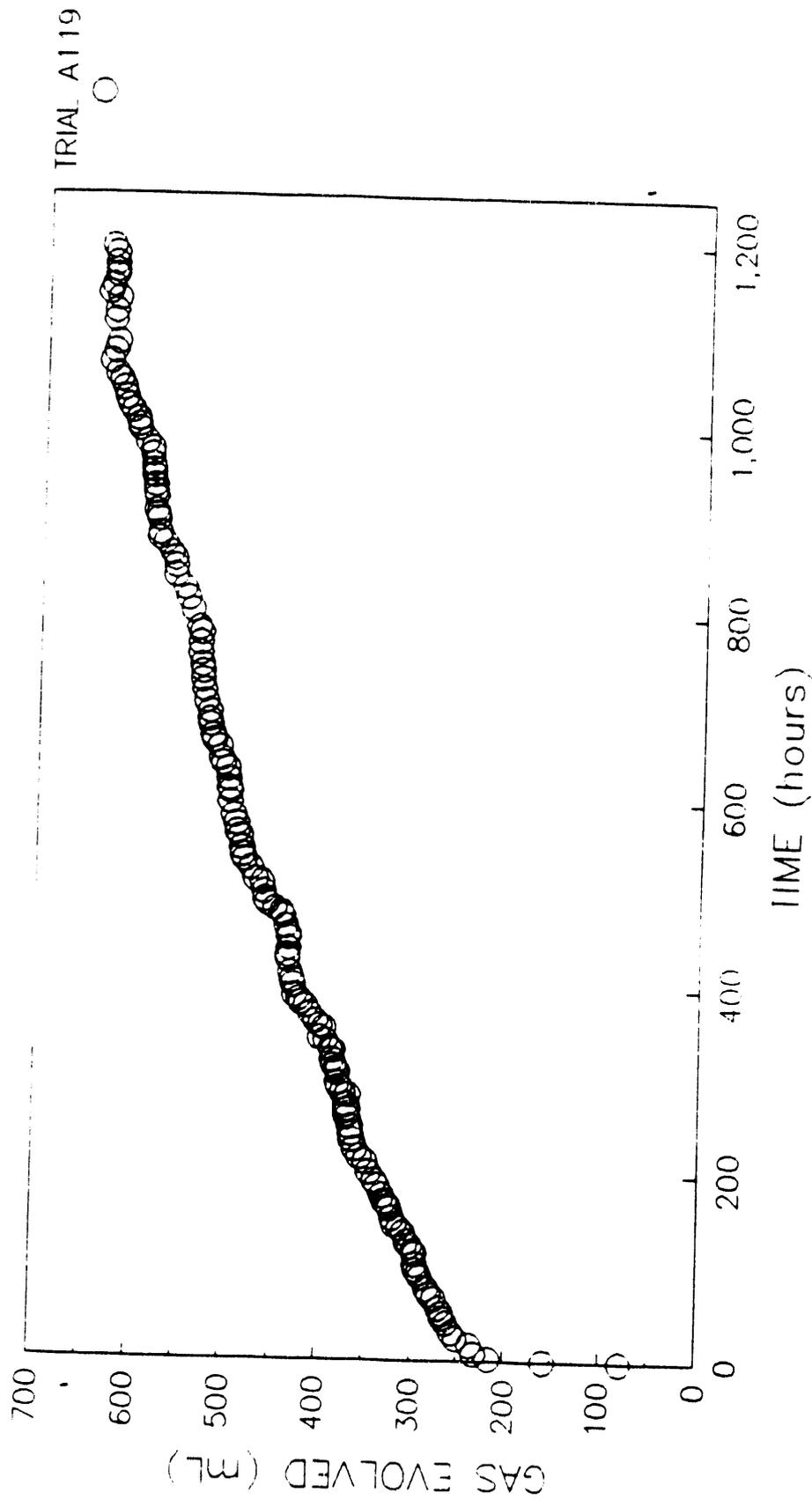
GAS EVOLUTION TRIAL A97
EXPANSION OF 300 TO 550 HOUR PLOT
MEDTA UNDER AIR WITH SONICATION



reaction apparatus 2

uncorrected for temperature and pressure

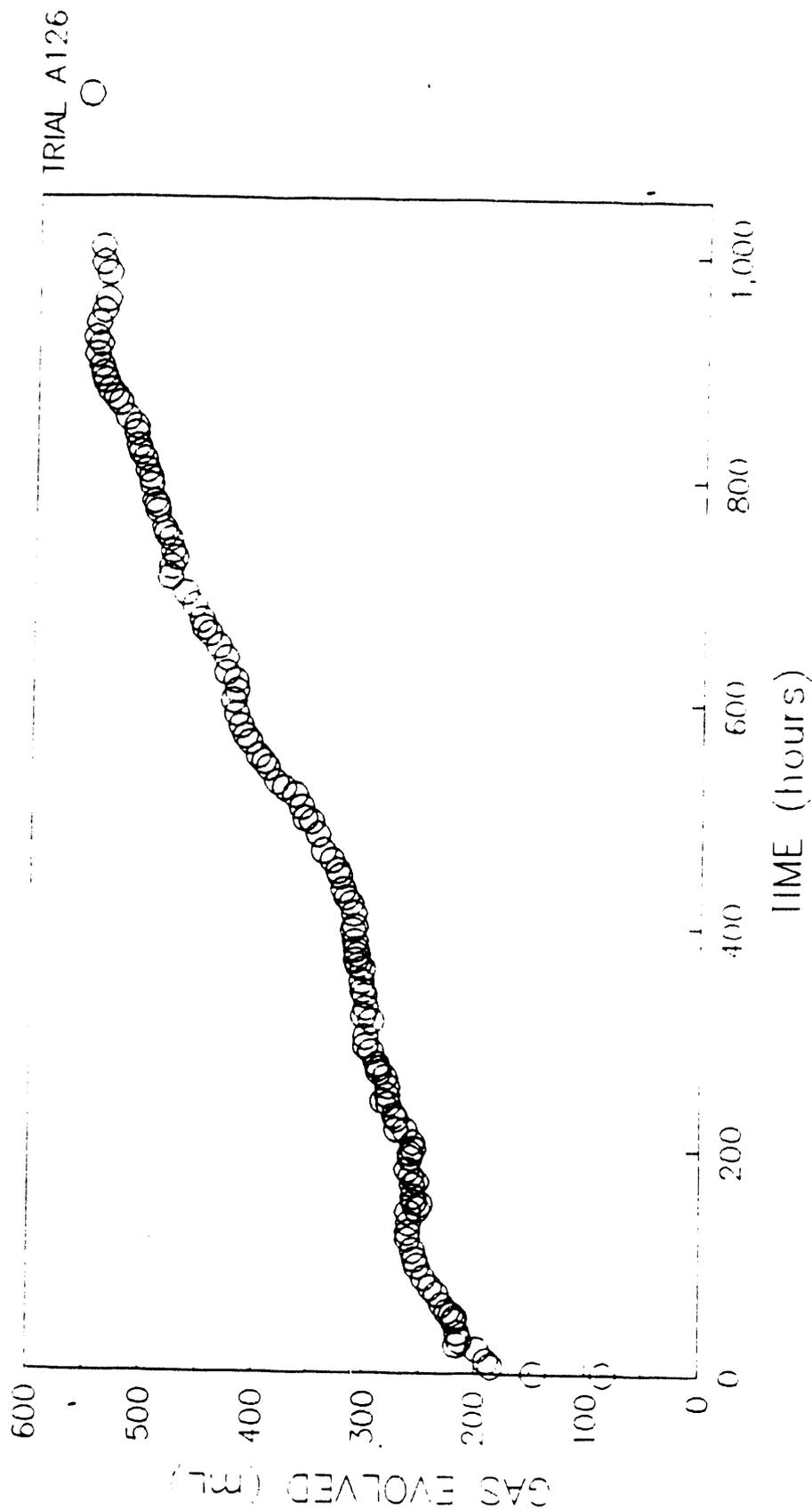
GAS EVOLUTION TRIAL A119
HOMOGENEOUS CONDITIONS & DEOXYGENATED WATER
GLYCOLIC ACID UNDER HELIUM ATMOSPHERE



reaction apparatus 6

uncorrected for temperature and pressure

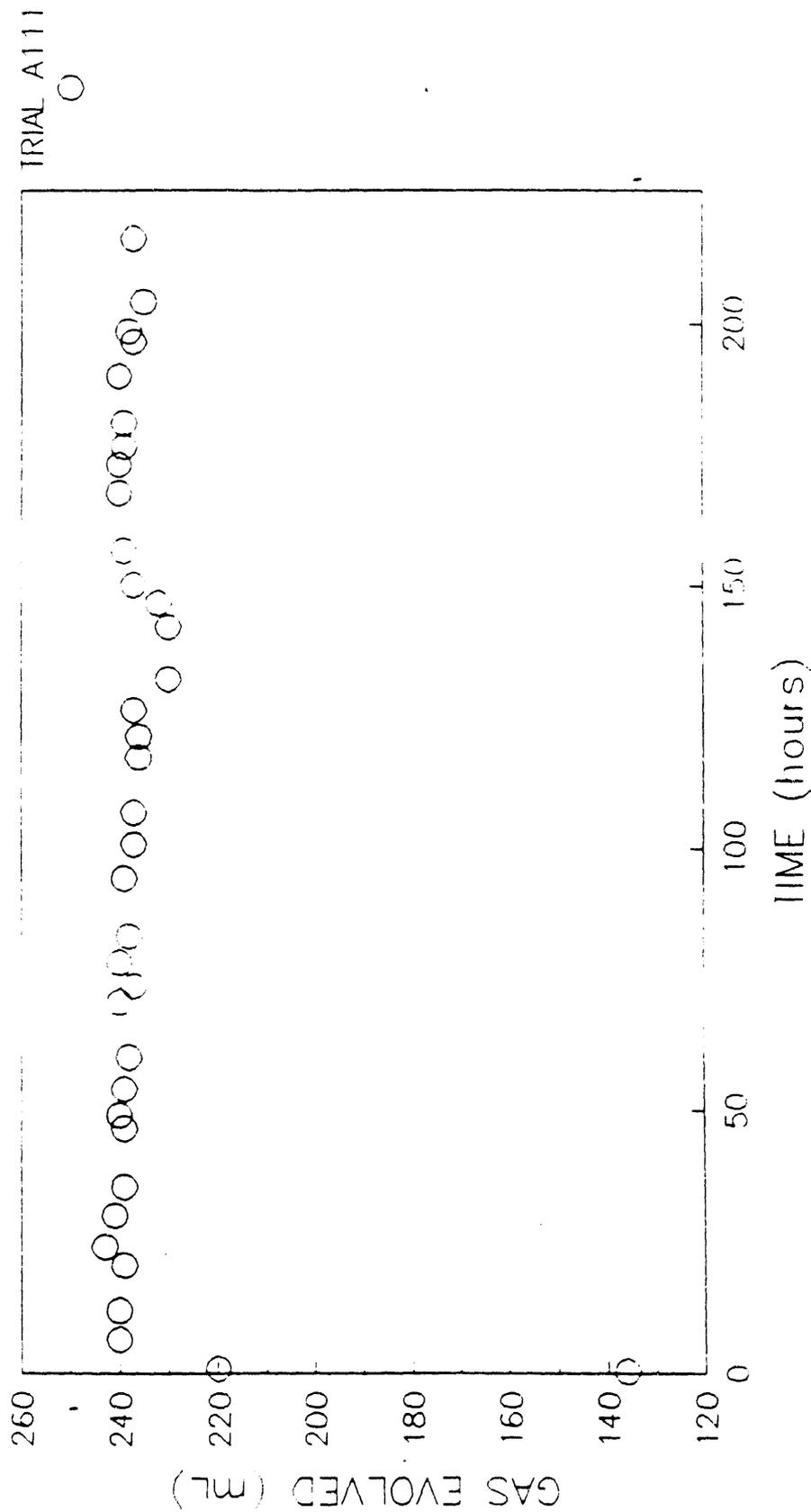
GAS EVOLUTION TRIAL A126
HOMOGENEOUS CONDITIONS
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus ?
vessel popped open

uncorrected for temperature and pressure

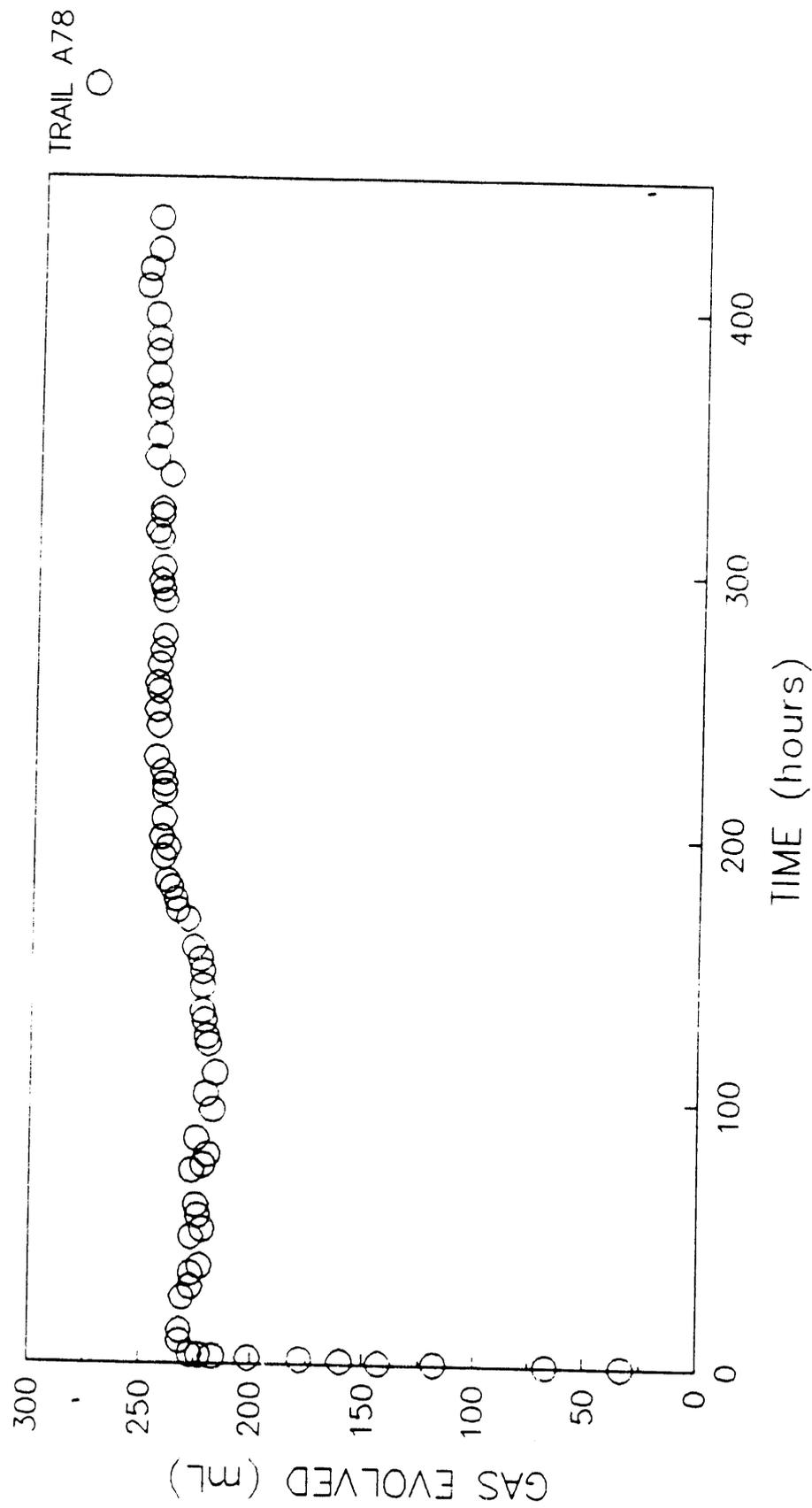
GAS EVOLUTION TRIAL A111
HOMOGENEOUS CONDITIONS WITHOUT SODIUM ALUMINATE
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus 5

uncorrected for temperature and pressure

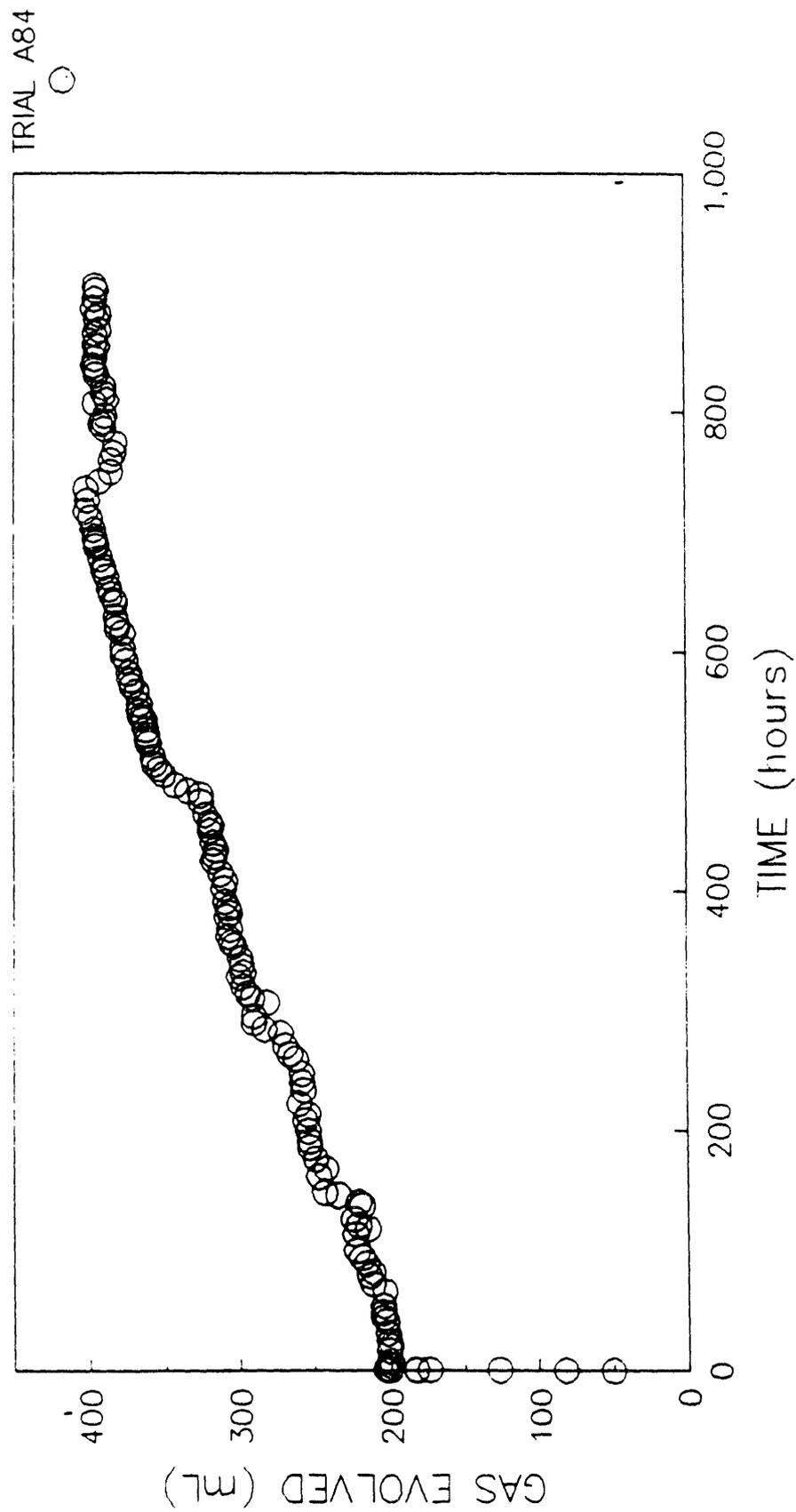
GAS EVOLUTION TRIAL A78
HOMOGENEOUS CONDITIONS WITHOUT SODIUM NITRITE
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus 5

uncorrected for temperature and pressure

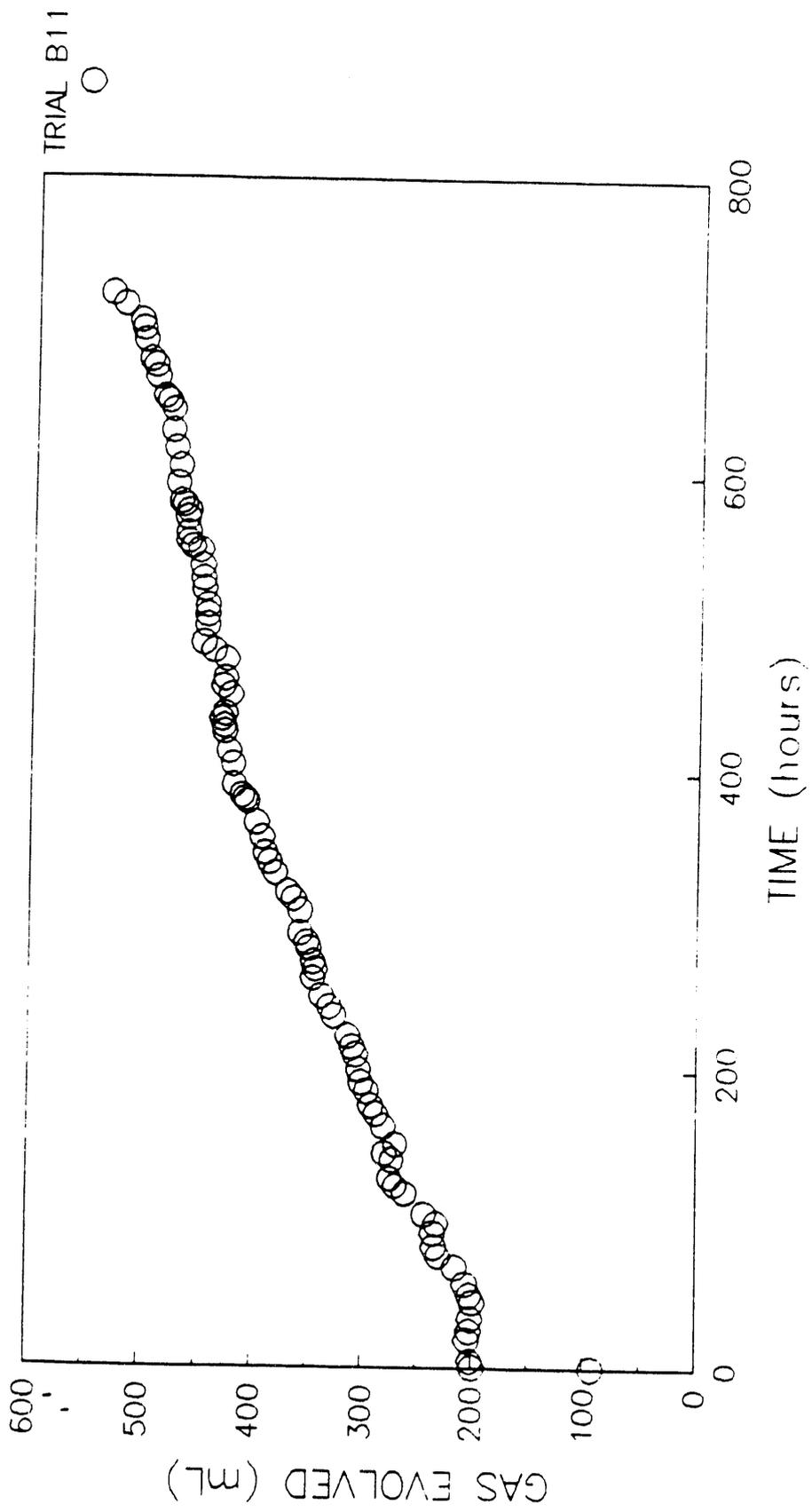
GAS EVOLUTION TRIAL A84
HOMOGENEOUS CONDITIONS WITHOUT SODIUM NITRATE
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus 3

uncorrected for temperature and pressure

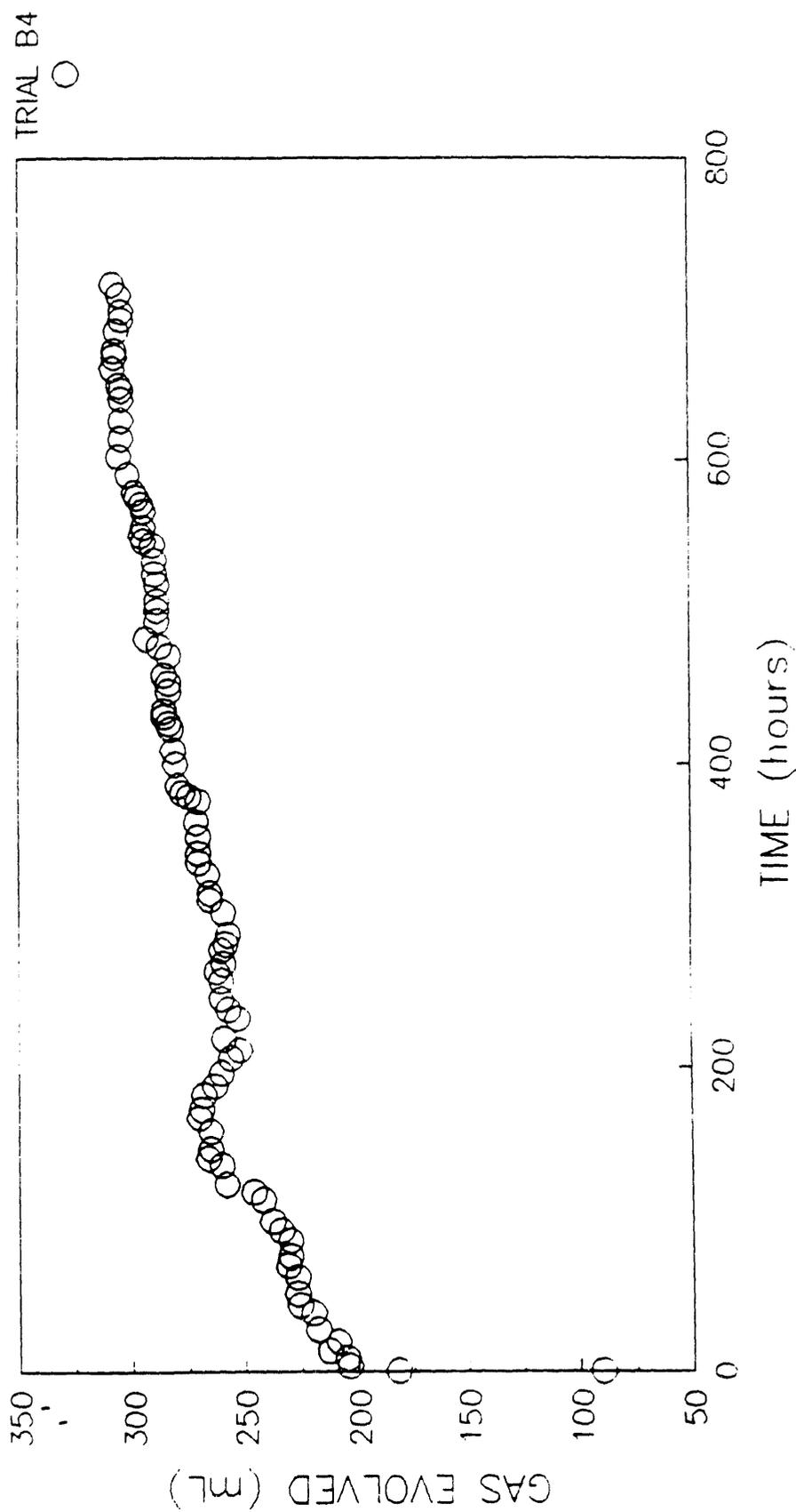
GAS EVOLUTION TRIAL B11
HOMOGENEOUS CONDITIONS WITH CHROMIUM CATALYSTS
GLYCOLIC ACID UNDER HELIUM ATMOSPHERE



reaction apparatus 1

uncorrected for temperature and pressure

GAS EVOLUTION TRIAL B4
HOMOGENEOUS CONDITIONS WITH CHROMIUM CATALYSTS
GLYCOLIC ACID UNDER AIR ATMOSPHERE



reaction apparatus 3

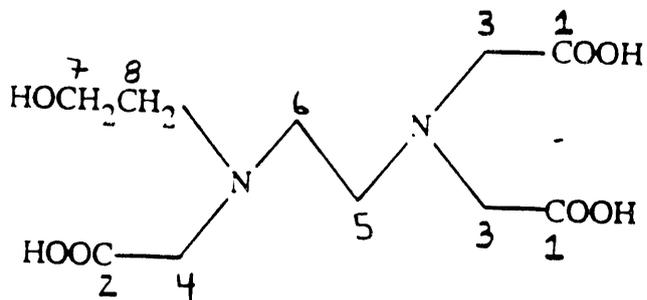
uncorrected for temperature and pressure

EXPERIMENTAL OBSERVATIONS CONCERNING NONVOLATILE PRODUCT FORMATION

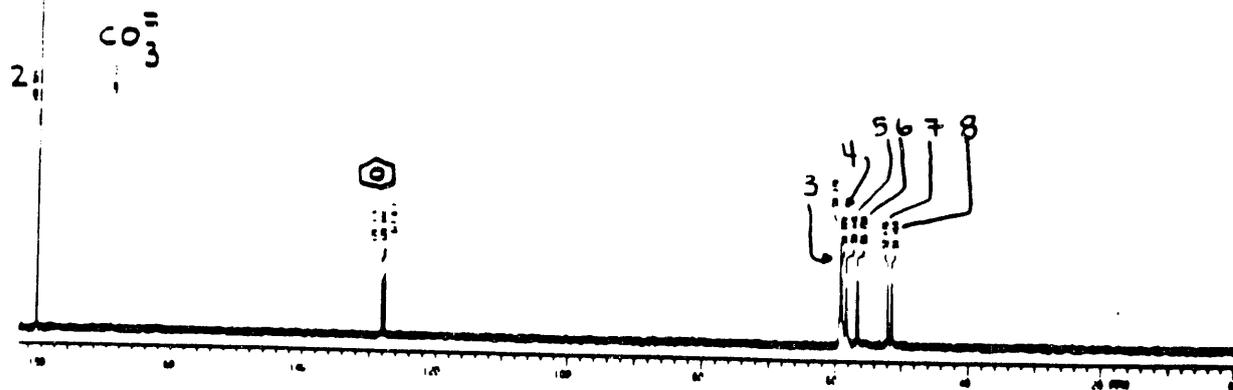
- 1) A ^{13}C database has been established for the identification of the organic degradation products. The ^{13}C NMR spectra of experiments using HEDTA or glycolate as the organic component under an air atmosphere, along with their initial "final word" mixtures are shown.

EXPERIMENT A50

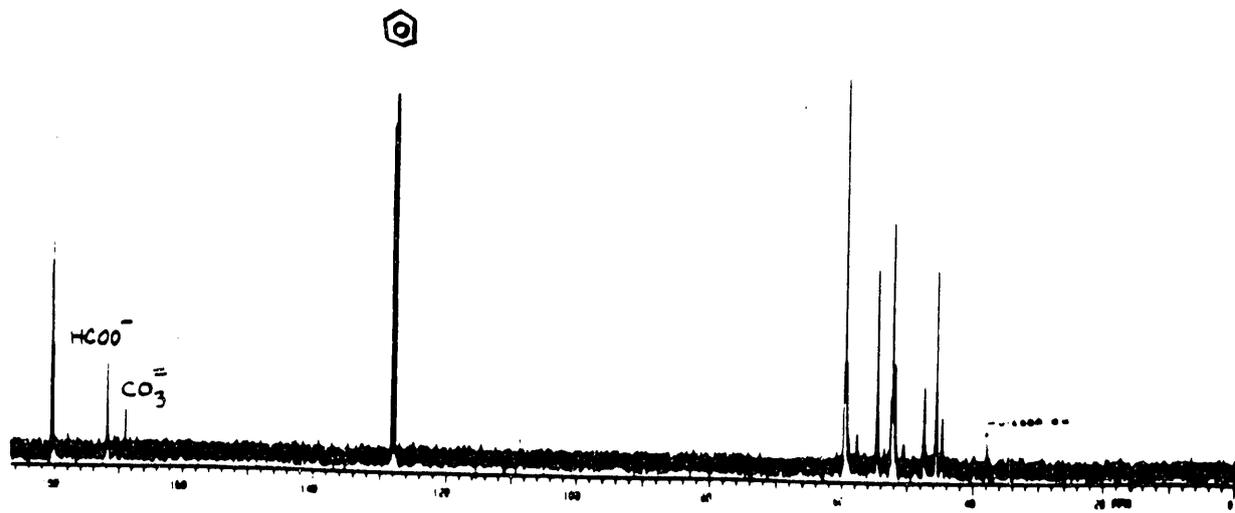
BEFORE



HEDTA

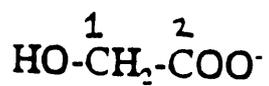


AFTER

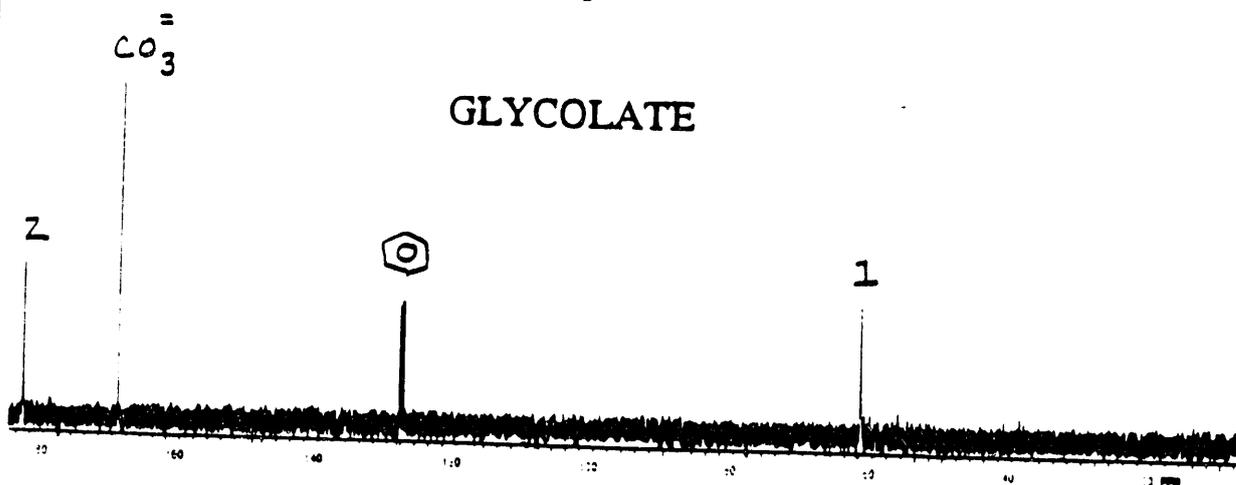


EXPERIMENT A 84

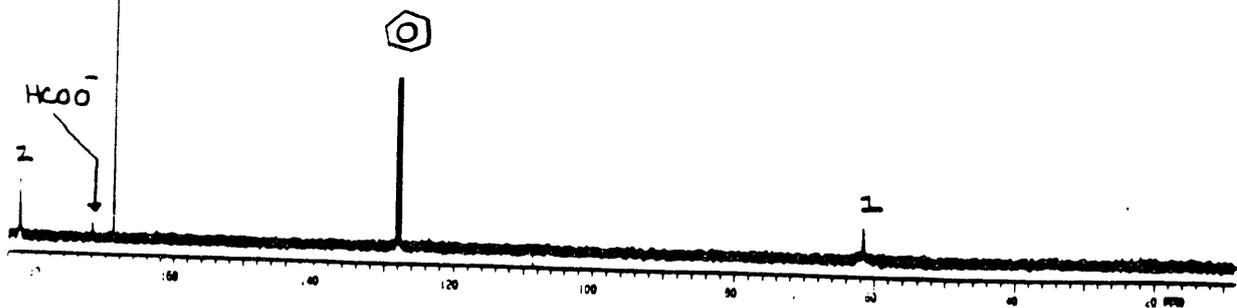
BEFORE



GLYCOLATE

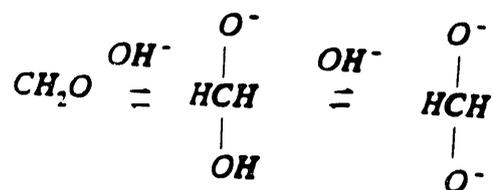
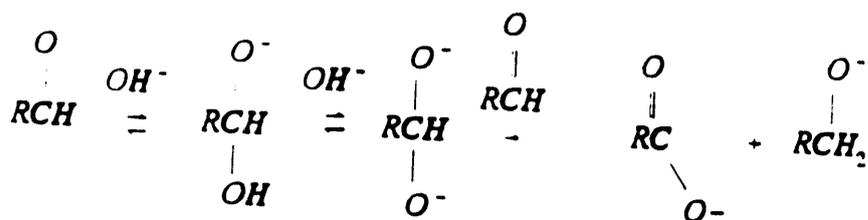
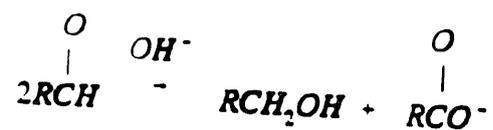


AFTER



HYDROGEN GENERATION FROM FORMALDEHYDE

The Cannizzaro Reaction.

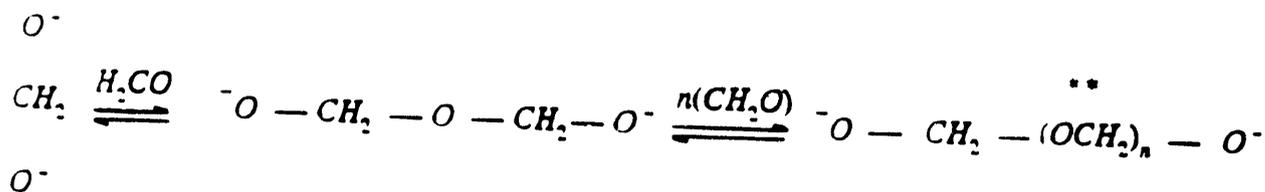


The Cannizzaro Intermediate.



¹³C-NMR and ¹⁷O-NMR Shifts of CH₂O

δ(ppm)	CH ₂ O\H ₂ O	CH ₂ O\OH ⁻	(CH ₂ O) _n \H ₂ O	(CH ₂ O) _n \OH ⁻
¹³ C-NMR	81.6	85.2 (broad)	81.5	85.4(broad)
¹⁷ O-NMR	51.0	68.0		



Reaction of p-nitrobenzaldehyde (p-NO₂PhCHO) in D₂O/OD⁻

Solvent	p-NO ₂ PhCHO	p-NO ₂ PhCH(OH) ₂	p-NO ₂ PhCH ₂ OH	p-NO ₂ PhCOONa
D ₂ O	82 %	18 %		
D ₂ O/OD ⁻		47%*	26%	26%

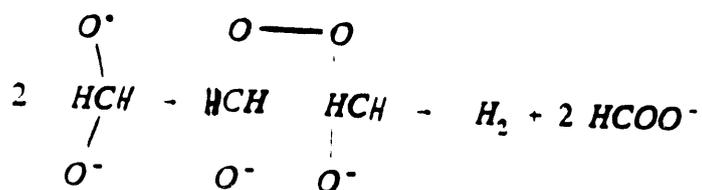
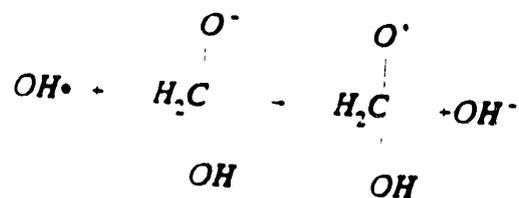
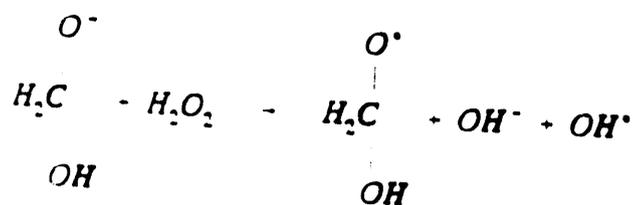
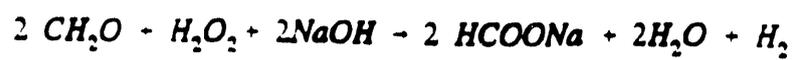
Hydrogen Evolution



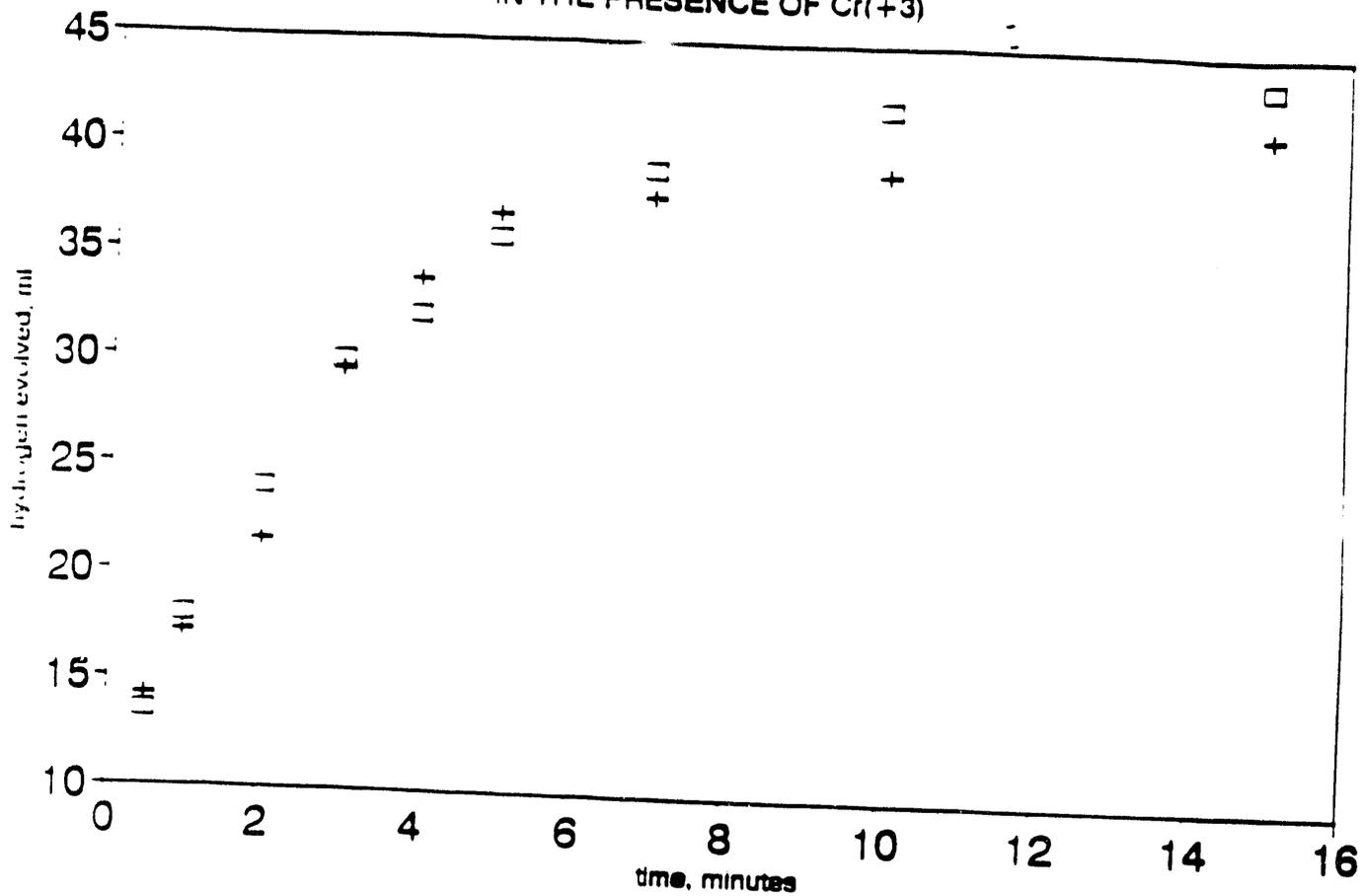
The Cannizzaro Reaction of CH₂O. Effect of H₂O₂. [CH₂O] 0.2M. r.t.]

Time (hrs.)	10% H ₂ O ₂ ^a		50% H ₂ O ₂ ^a	
	%HCOO ⁻	%CH ₂ OH	%HCOO ⁻	%CH ₂ OH
0.5	23.1	traces	66.4	0
3	21.0	3.7	87.3	0
24	26.3	15.5	109.4	0
48	30.5	19.4	96.0	0

^aPercentage based on CH₂O.

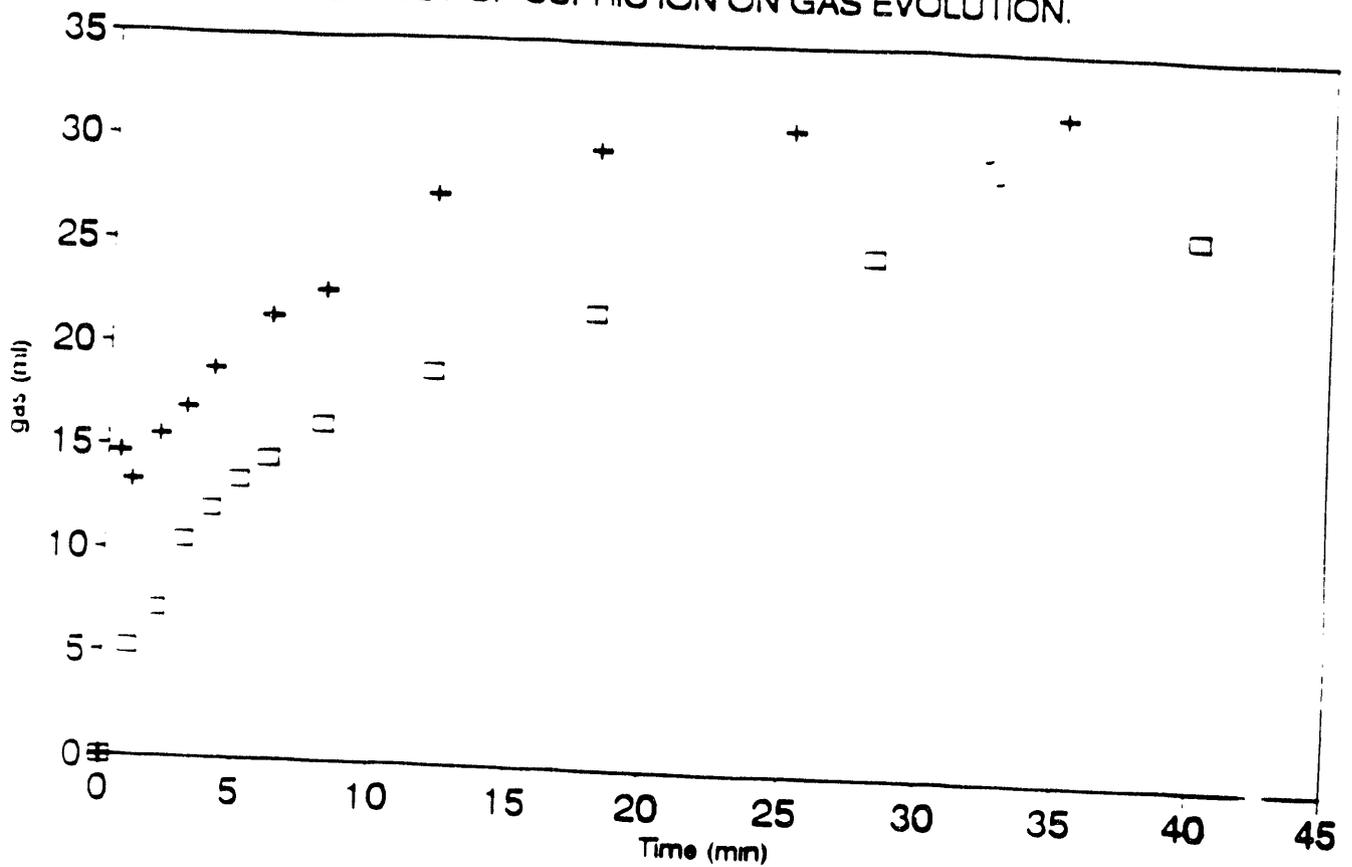


REACTION OF FORMALDEHYDE WITH BASE
IN THE PRESENCE OF Cr(+3)

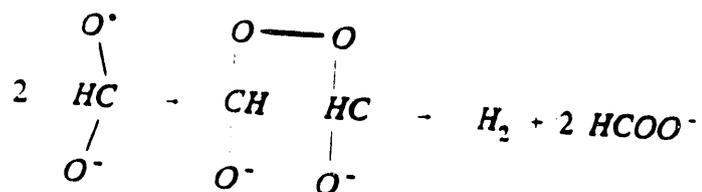
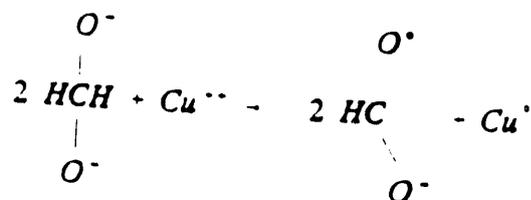
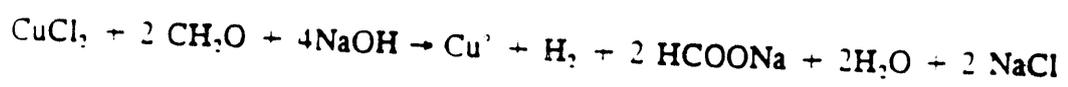


— control + Cr(+3) added

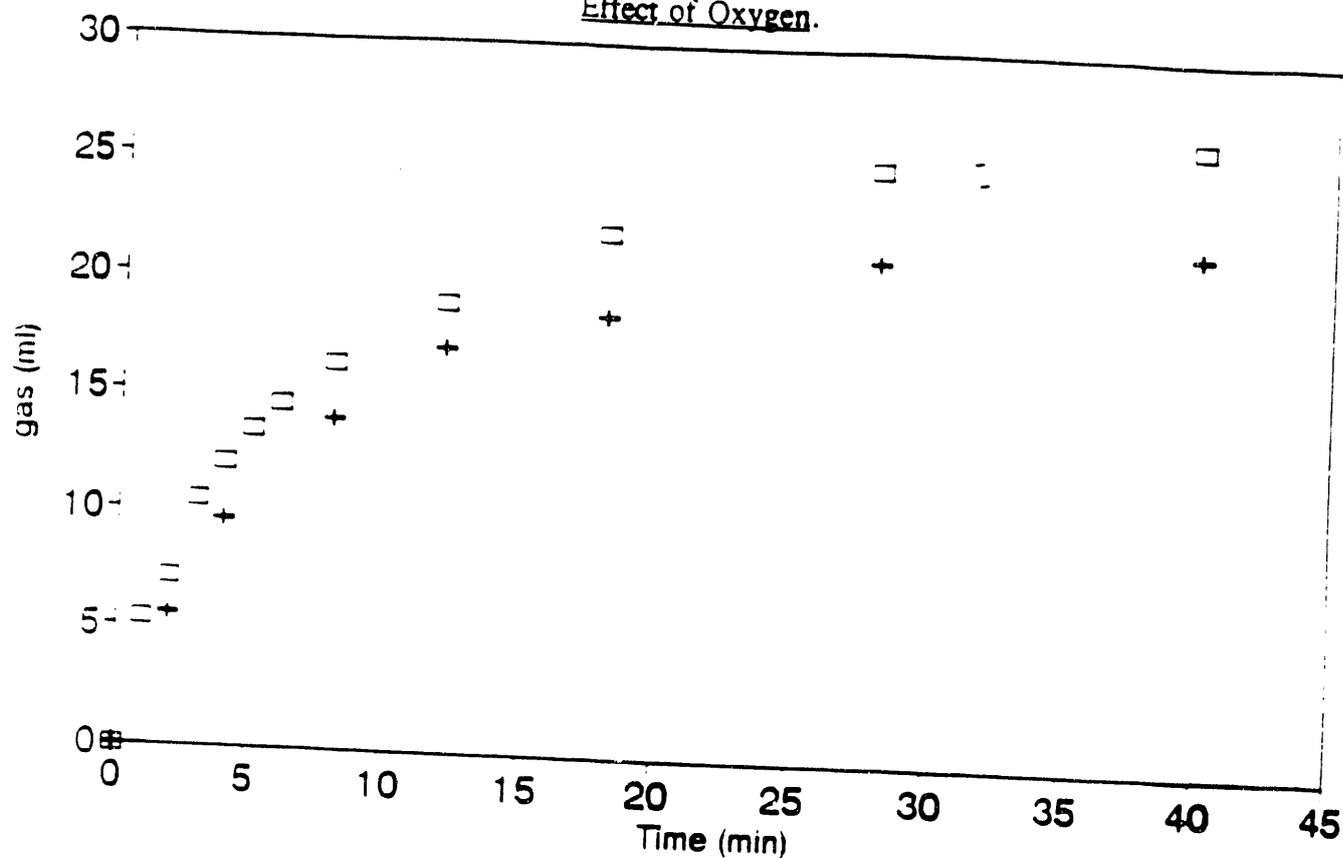
REACTION OF FORMALDEHYDE WITH BASE.
EFFECT OF CUPRIC ION ON GAS EVOLUTION.



□ Normal + Cupric ion



REACTION OF FORMALDEHYDE WITH BASE.
Effect of Oxygen.



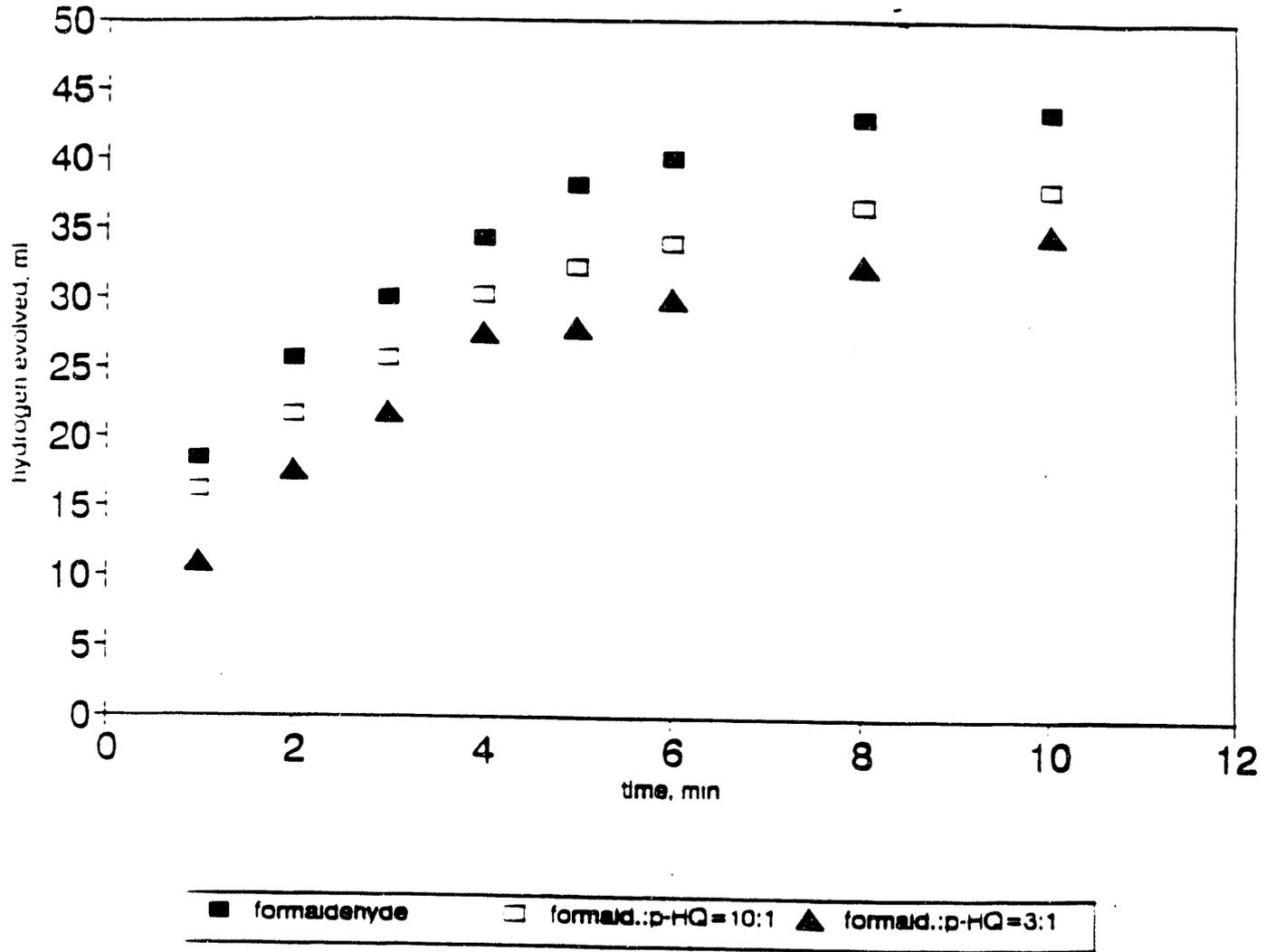
□ Nitrogen + Oxygen
+ Nitrogen

Hydrogen Evolution from CH_2O . Yield of Gas Under Different Atmospheres

Atmosphere	O_2	air	N_2
Gas Evolved (ml)	16.3	19.6	22.3
Time (min.)	51	45	54
Yield of gas (%)	34	42	48

Effect of a Radical Inhibitor.

REACTION OF FORMALDEHYDE WITH BASE
IN THE PRESENCE OF p-HYDROQUINONE



Effect of Base Concentration and Temperature on Hydrogen Yield.

	T.(°C)	[CH ₂ O],M	[NaOH],M	% HCOONa	% CH ₂ OH	% H ₂
1	60	0.05	15	55.2	36.4	14.2
2	60	0.05	3	51.2	40.6	0.1
3	90	0.017	17	71.3	27.0	41.1
4	90	0.017	17	76.0	21.6	43.1
5	90 ^a	0.017	17	70.0	16.2	41.6
6	120	0.05	2	54.6	45.4	2.1
7	120	0.05	2("final word") solution	65.2	40.2	3.4 ^b

^aCrCl₃ added ((CrCl₃) = 0.002M. ^bN₂O was also observed (2.4% based on CH₂O)

Deuterium Tracer Studies

Reaction of CH_3O in $\text{D}_2\text{O}\backslash\text{OD}^-$

	T, °C	[CH_3O], M	[NaOD], M	% CH_3OH	% HCOONa	H_2 :HD:D ₂			Total % Hydrogen
1	90	0.055 ^a	16	44.6	64.0	23	16	100	15.9
2		blank ^b	16			100	11	1	
3		0.062 ^c	16	60.4	54.2	10	18	100	9.7
4		blank ^b	16			100	5	0	
5		blank ^d	16			12	100	4	
6	60	0.050	15	35.0	34.0	100	7	22	14.2 ^e
7		0.050	15			100	14	78	
8		0.050 ^e	15	25.6	24.6	100	7	61	
9		0.120 ^f	15	34.8	32.3	100	28	33	
10	60	0.018	3	49.4	48.2	100	13	14	0.1 ^g
11		blank ^b	3			100	2	2	
12		blank ^d	3			17	100	13	
13		0.05	3	39.0	44.0	100	22	55	
14		0.05	3	41.6	37.0	100	43	40	
15	25	0.20 ^e	15	41.8	46.2	100	3	1	1.9 ^g

- a. CH_3O added in 3 aliquots. Reaction time: 40 min.
- b. H_2 was bubbled into the basic solution
- c. CH_3O added all at once. Reaction time: 5 min.
- d. A mixture $\text{LiAlH}_4\backslash\text{D}_2\text{O}\backslash\text{NaOD}$ was used (HD was the only gas expected)
- e. This reaction was carried out in a glass vessel (all the others were done in teflon vessels).
- f. The M.S. technique used in this case was different: a gas aliquot of the sample was injected with a syringe while in the other cases the whole headspace was removed.
- g. Measured for $\text{CH}_3\text{O}\backslash\text{OH}\backslash\text{H}_2\text{O}$.

Hydrogen Evolution from Aldehydes Other than CH₂O.

Aldehyde	% RCOONa	% RCH ₂ OH	% H ₂
benzaldehyde	~ 0 ^b	traces ^b	16.9
glyoxalate	? ^c	34.1	29.0
formaldehyde ^d	71.3	27.0	41.1
pivaldehyde	(TO BE DONE)		

T = 90°C. (NaOH) = 16.7 M, (RCHO) = 0.017 M, in all cases

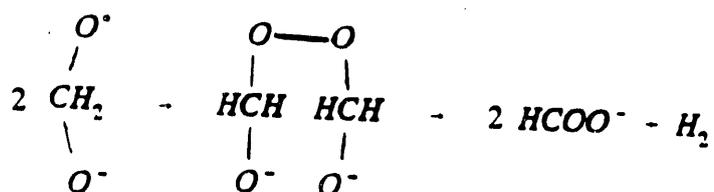
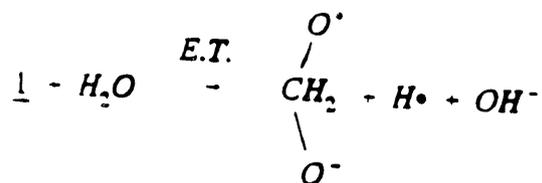
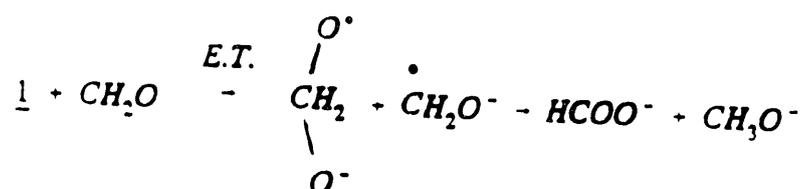
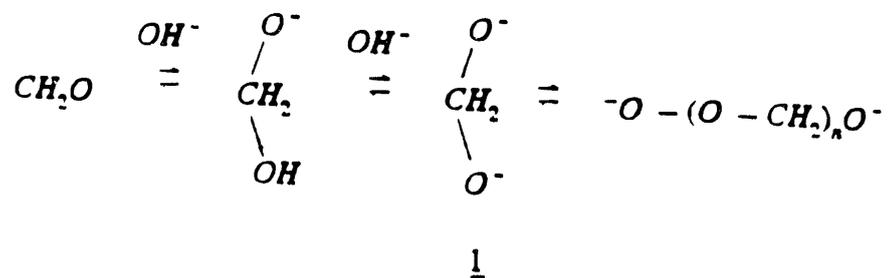
The main product was unidentified solid. No RCOONa or RCH₂OH were found by ¹H-NMR. Traces of RCH₂OH were observed by GC.

The acid salt precipitated as a solid. The yield has to be determined.

Included for comparison.



PROPOSED MECHANISM.



Decomposition of C-13 Labeled HEDTA (HO¹³CH₂¹³CH₂-)**Objective:**

To determine products derived from loss of hydroxyethyl group.

Synthesis of labeled compound:

Alkylation of H₂NCH₂CH₂NH¹³CH₂¹³CH₂OH (from 1,2-diaminoethane and ethylene oxide) with BrCH₂CO₂H.

Experiment:

Heat simulated waste mixture prepared with labeled HEDTA and monitor ¹³C NMR spectrum. Intensities measured relative to external benzene-d₆.

Observations:

Only formate and CO₂ (as carbonate) are observed as products.

Conclusions:

Long lived C₂ fragments, if formed, do not accumulate.

Two different C₁ products are formed. HCO₂⁻ is stable under the reaction conditions so that carbonate must arise by an independent pathway.

MeED3A is not formed by a thermal pathway.

Decomposition of C-13 Labeled Glycolate
 $HO^{13}CH_2^{13}CO_2^-$

Objective:

To determine products derived from glycolate *in situ*.

Experiment:

Heat simulated waste mixture prepared with labeled acid and monitor ^{13}C NMR spectrum. Intensities measured relative to external benzene- d_6 .

Observations:

Evidence for complexation of glycolate by aluminum; necessity of aluminum for decomposition not yet determined.

Formate, oxalate and carbonate are observed as products.

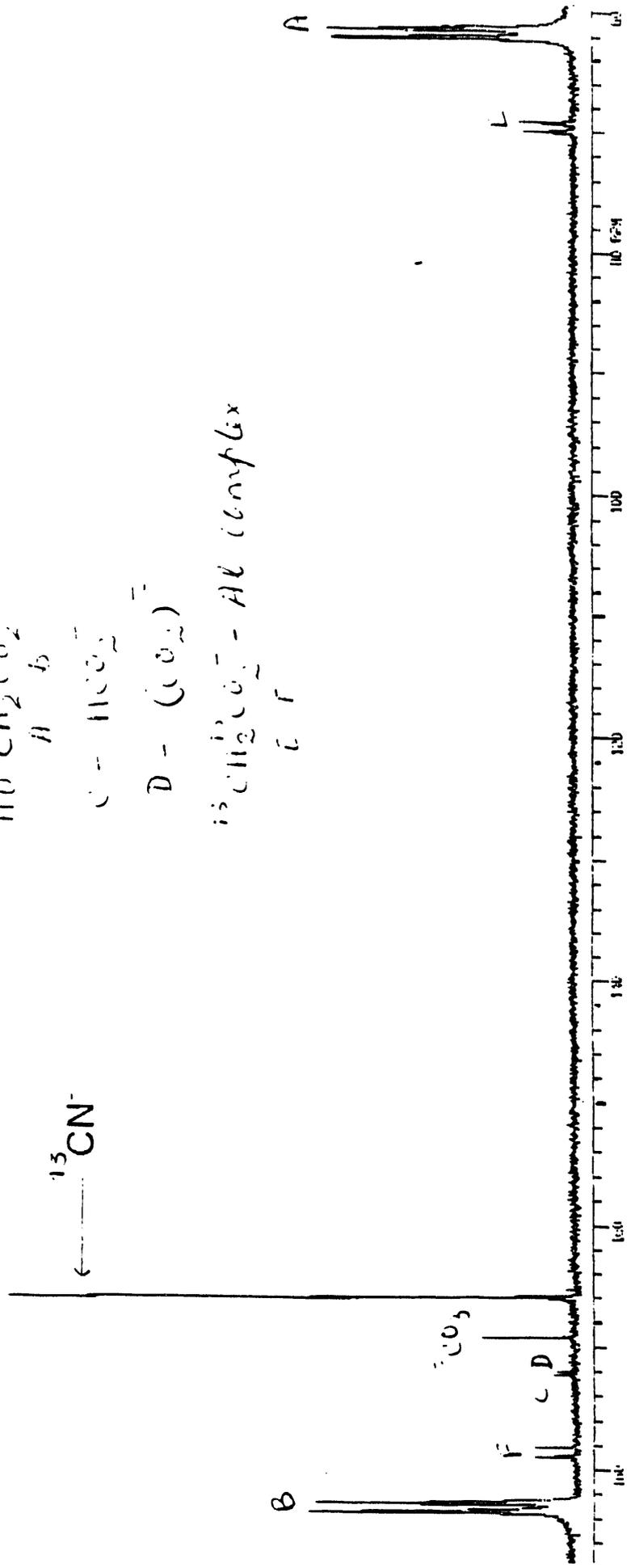
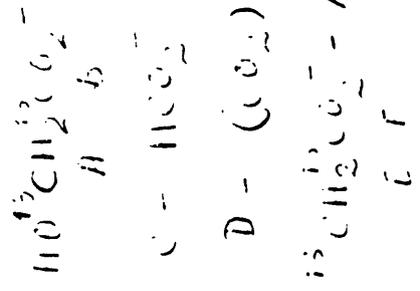
Conclusions:

Products observed are consistent with postulated mechanism for reaction with nitrite.

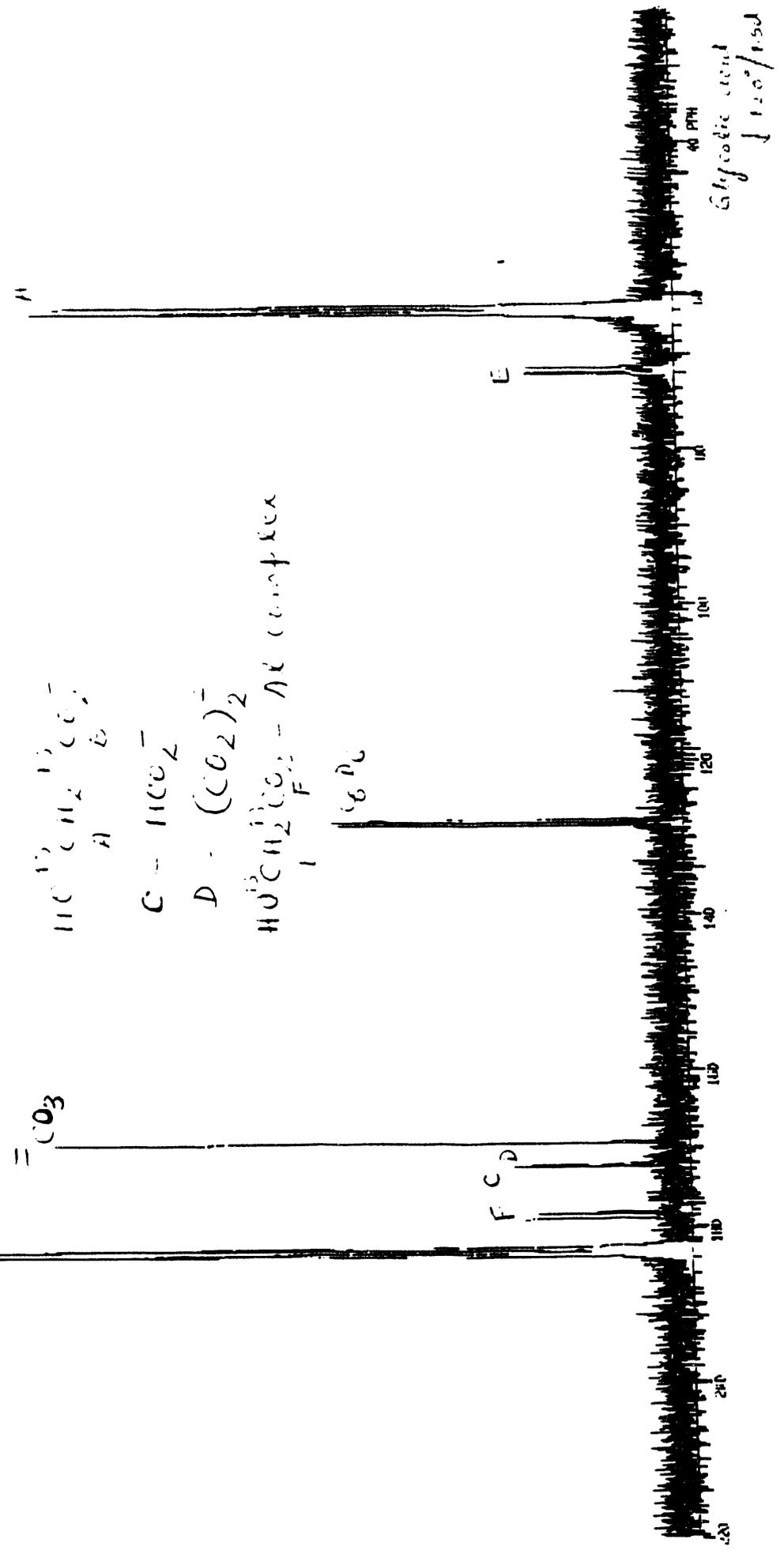
C-13 NMR of Labeled Glycolic Acid
no aluminum added to solution



C-13 NMR of Labeled Glycolic Acid
 15 h at 120°; external CN⁻ reference

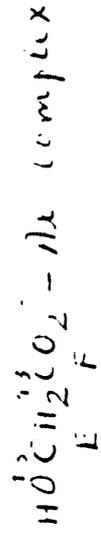
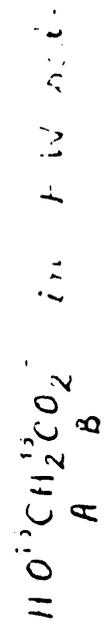


C-13 NMR of Labeled Glycolic Acid
 1.5 days at 120°; external C₆D₆ reference

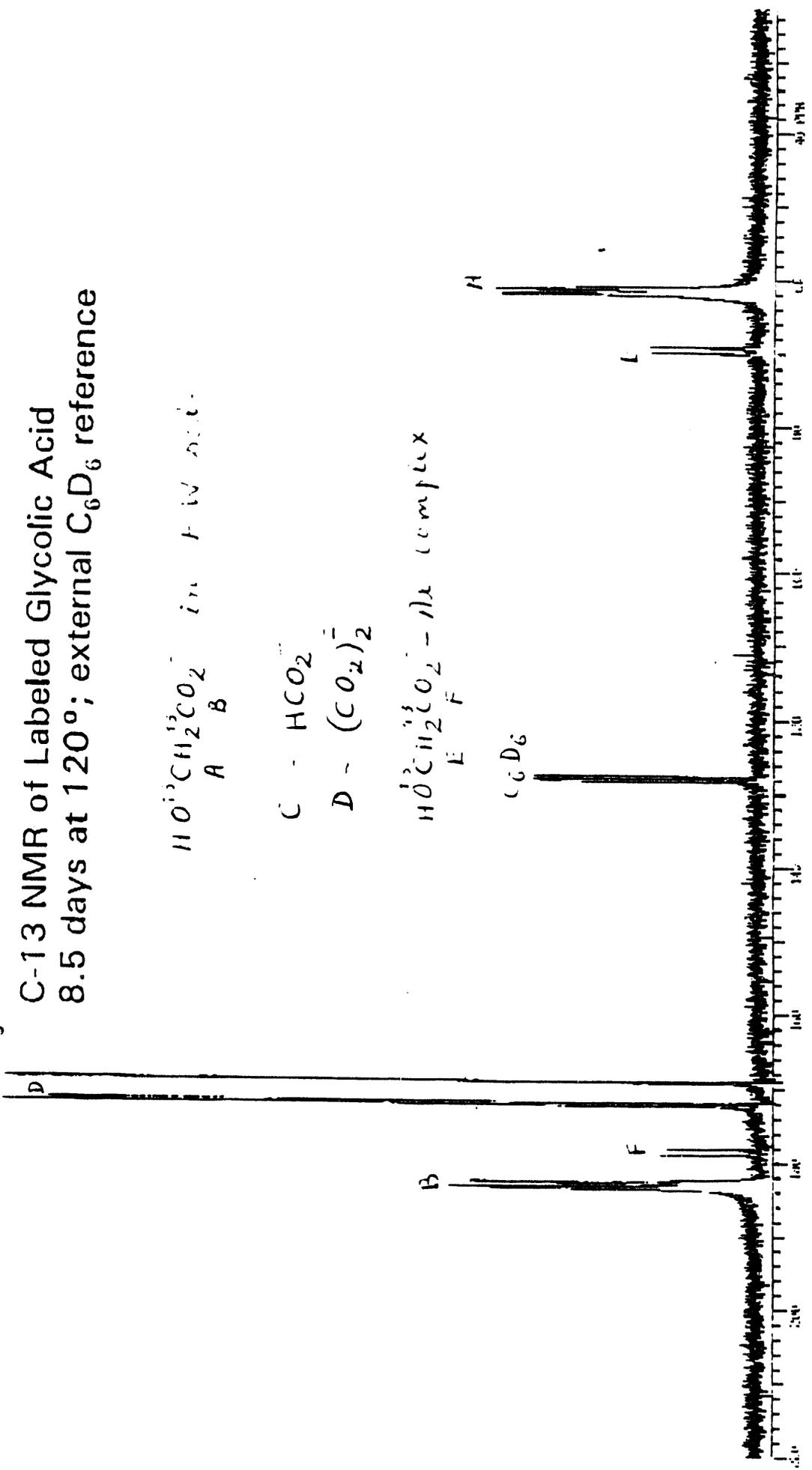


C $\bar{C}O_3$

C-13 NMR of Labeled Glycolic Acid
8.5 days at 120°; external C_6D_6 reference



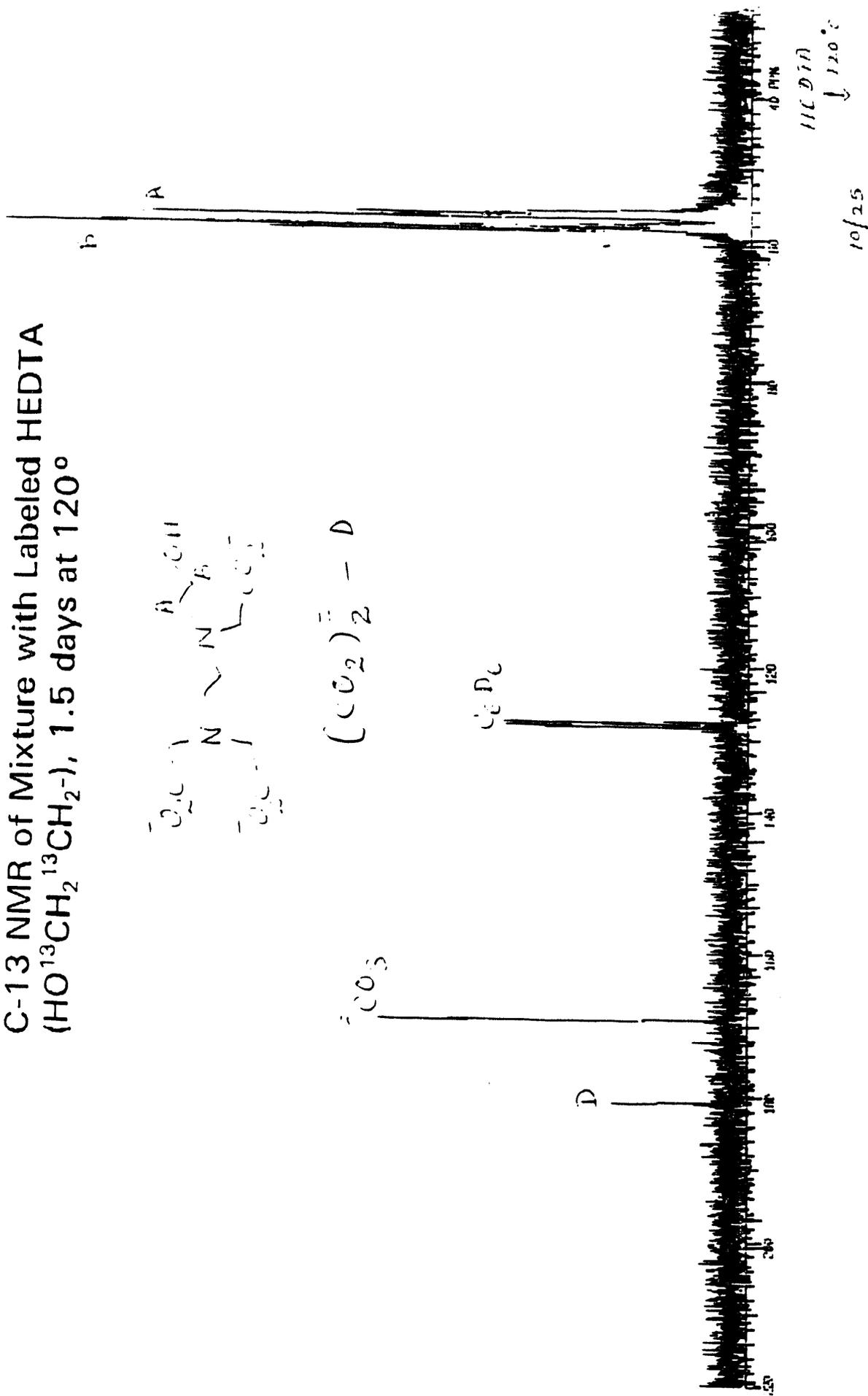
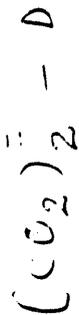
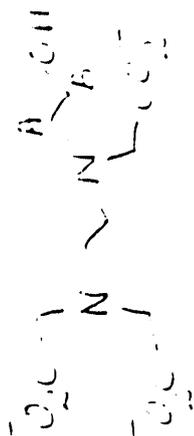
C_6D_6



Glycolic acid
120°C

1050
Scale

C-13 NMR of Mixture with Labeled HEDTA
 (HO¹³CH₂¹³CH₂⁻), 1.5 days at 120°

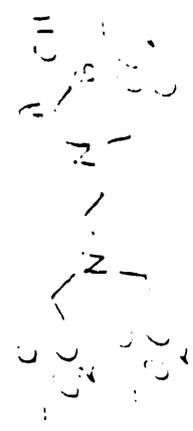
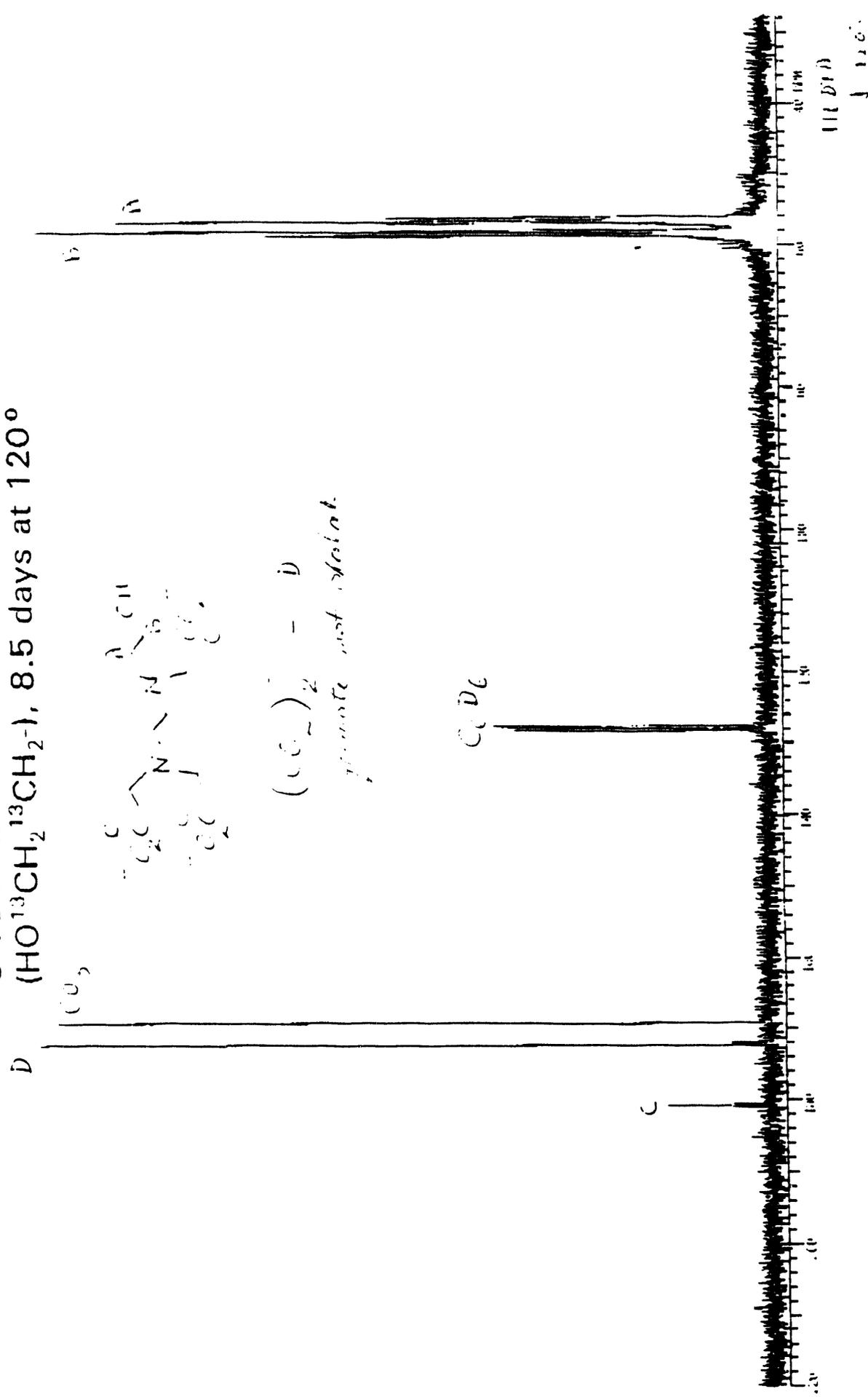


HEDTA
 ↓ 120°

10/25

with CO₂

C-13 NMR of Mixture with Labeled HEDTA
 (HO¹³CH₂¹³CH₂-), 8.5 days at 120°



(CO₂)₂ = D
 separate not shown

LITERATURE SEARCH

A brief, selective (and certainly incomplete) literature search has been made to acquaint ourselves with some of the redox chemistry of nitrogen that may be important in our experiments. This survey covers reactions occurring in the absence of radiation.

Topics examined:

Oxidation-Reduction Potentials

Reduction of Nitrate and Nitrite

Nitrosyl Hydride (more commonly known as "Nitroxyl")

Trans-Hyponitrous Acid and Hyponitrites

Cis-Hyponitrite

Hyponitric Acid and Hyponitrates

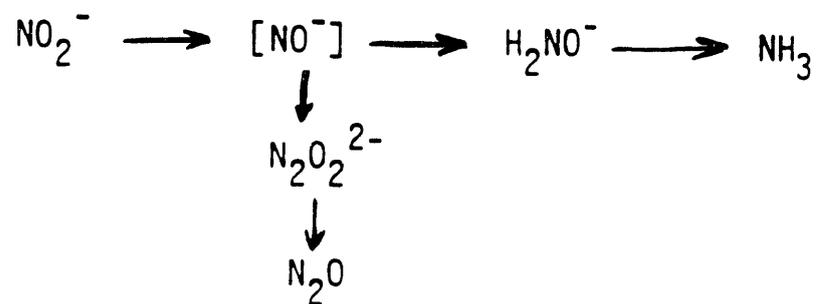
Reactions of Hydroxylamine

Peroxynitrous Acid, HOONO , and Peroxynitrite

SOME GENERALIZATIONS FROM LITERATURE SEARCH

In both acidic and basic solutions NO_3^- is kinetically much less reactive than NO_2^-

Reduction of NO_2^- in basic solution leads to observed products along the sequence



NO^- is a product inferred, not observed

In the absence of other reactants, the following species have measurable life-times (greater than minutes at 25°C) in 1 M NaOH:

Trans-hyponitrite, $\text{N}_2\text{O}_2^{2-}$

Hyponitrate, $\text{N}_2\text{O}_3^{2-}$

Conjugate base of hydroxylamine, H_2NO^-

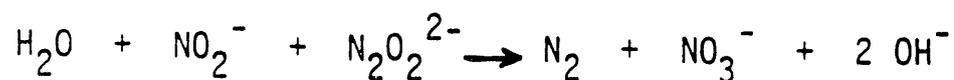
These species are more stable than their conjugate acids, which accounts for the greater stability in alkaline solution.

Although their concentrations may not be high in the tank, their steady-state concentrations could be higher than that of more transient intermediates.

Almost certainly NO^- (singlet and/or triplet) is an important intermediate in our experiments (and in the waste tank).

Cis- and Trans- $\text{N}_2\text{O}_2^{2-}$ may be intermediates in the formation of N_2O

A possible route to formation of N_2 would be



written solely in analogy to the reaction occurring in acidic solution. The possibility of this reaction in basic solution should be investigated.

If H_2NO^- is formed, there are two known reactions that can give N_2 and N_2O in basic solution

(1) Disproportionation to give N_2 , N_2O , and NH_3

[But this reaction gives more NH_3 than N_2 and N_2O]

(2) Reaction of H_2NO^- with NO to give N_2 and N_2O

[Requires that NO be formed by $1 e^-$ reduction of NO_2^-]

[Gives N_2 and N_2O in a 1:1 ratio ; nearly the tank ratio]

ANALYSIS FOR ANIONS

Ion-Chromatography(IC)

We are analyzing for the following anions, using a Dionex DX-300

Series Chromatograph: Formate
 Glycolate
 Glyoxylate
 Oxalate
 Nitrite
 Nitrite

Ultra-violet Spectrophotometry(UV)

We are also analyzing for NO_2^- and NO_3^- by using absorption at 302 nm and 354 nm.

At 354 nm NO_2^- has an absorption maximum, with $\epsilon = 23.0$

At 302 nm NO_3^- has an absorption maximum, with $\epsilon = 7.20$, and

NO_2^- has a somewhat greater absorption, $\epsilon = 9.06$

Measurements at both wave-lengths necessary in the analysis.

Accurate determinations of the concentrations of nitrate and nitrite are especially important for mass-balance considerations. Thus we are concerned about agreement between concentrations determined by UV and IC. The table below compares results of analyses of samples obtained in various kinetic runs.

Sample	NaNO ₂ (Moles/250 ml)		NaNO ₃ (Moles/250 ml)	
	UV	IC	UV	IC
FWA*	0.221	0.212	0.254	0.260
A - 50 HEDTA/Air	0.169	0.151	0.250	0.255
A - 113 HEDTA/He	0.195	0.186	0.257	0.248
A - 126 Gly./Air	0.199	0.195	0.253	0.262
A - 119 Gly./He	0.195	0.194	0.254	0.258
A - 84 Gly./Air without NaNO ₃	0.203	0.200	-	-
B - 19 UEDDA/Air	0.218	0.224	0.254	0.257
B - 33 UEDDA/Air	0.217	0.220	0.252	0.276

FWA*: "final word" solution without organics after thermolyzing for 150 hours at 125 °C.

UEDDA: Unsymmetric EDDA.

Appendix I

Organic Methods Development and Preliminary Data for 101-SY

ORGANIC METHODS DEVELOPMENT
AND PRELIMINARY DATA FOR 101-SY

DR. J.A. CAMPBELL

ADVANCED ORGANIC-ANALYTICAL METHODS DEVELOPMENT
GROUP

PRESENTED BY

DR. R.M. BEAN

DISCUSSION

- CHARACTERIZATION OF WASTE
- AREAS OF METHODS DEVELOPMENT

CHELATORS

REMAINING TOC

- PRELIMINARY RESULTS OF DERIVATIZATION GC/MS OF 101-SY SAMPLE
- FURTHER STUDIES

IMPORTANCE OF CHARACTERIZATION OF WASTE

- PRODUCTION OF HYDROGEN
- SAFETY
- SENSOR DEVELOPMENT
- RISK AND ASSESSMENT
- ANY TYPE OF REMEDIATION
- MODELLING

TANK WASTE SCIENCE PANEL:

TANK 101-SY MUST BE PHYSICALLY AND CHEMICALLY CHARACTERIZED AS FULLY AS POSSIBLE AND EXPEDITIOUSLY AS SAFETY CONSIDERATIONS ALLOW

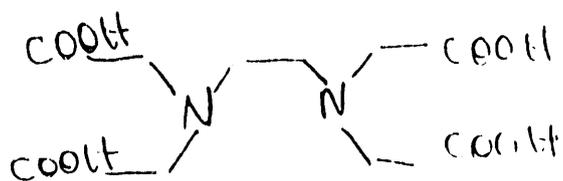
METHODS DEVELOPMENT

- PEROXIDES-HEXONE
- CHELATORS AND DEGRADATION PRODUCTS
 - DERIVATIZATION GC/MS
 - HPLC
 - LC/MS
 - ELECTROSPRAY/MS
- REMAINING TOC
- SYSTEMATIC APPROACH TO ANALYSIS SCHEME

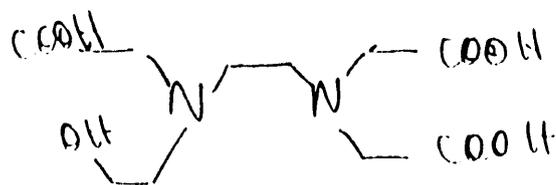
IMPORTANCE OF CHELATORS

- WATER SOLUBLE COMPLEXES
- ADDED TO WASTE TO COMPLEX RADIONUCLIDES
- POSSIBLE DEPOSITION IN GROUND WATER
- INCREASED MOBILITY THROUGH SOIL
- AFTER 40-50 YEARS OF RADIOLYTICAL & CHEMICAL DEGRADATION, FRAGMENTS MAY HAVE HIGHER COMPLEXING CAPABILITY

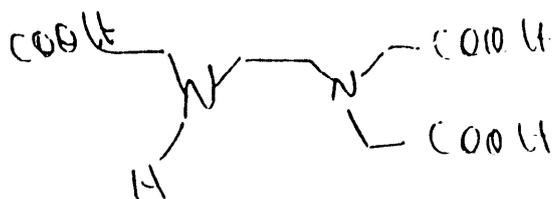
CHELATOR STRUCTURES



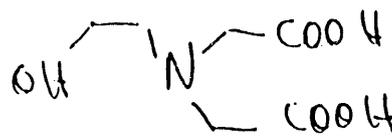
EDTA



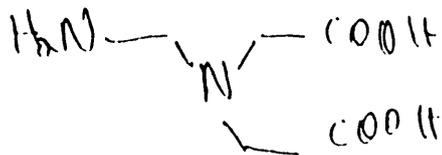
HEDTA



ED3A



HEIDA



NAIWA

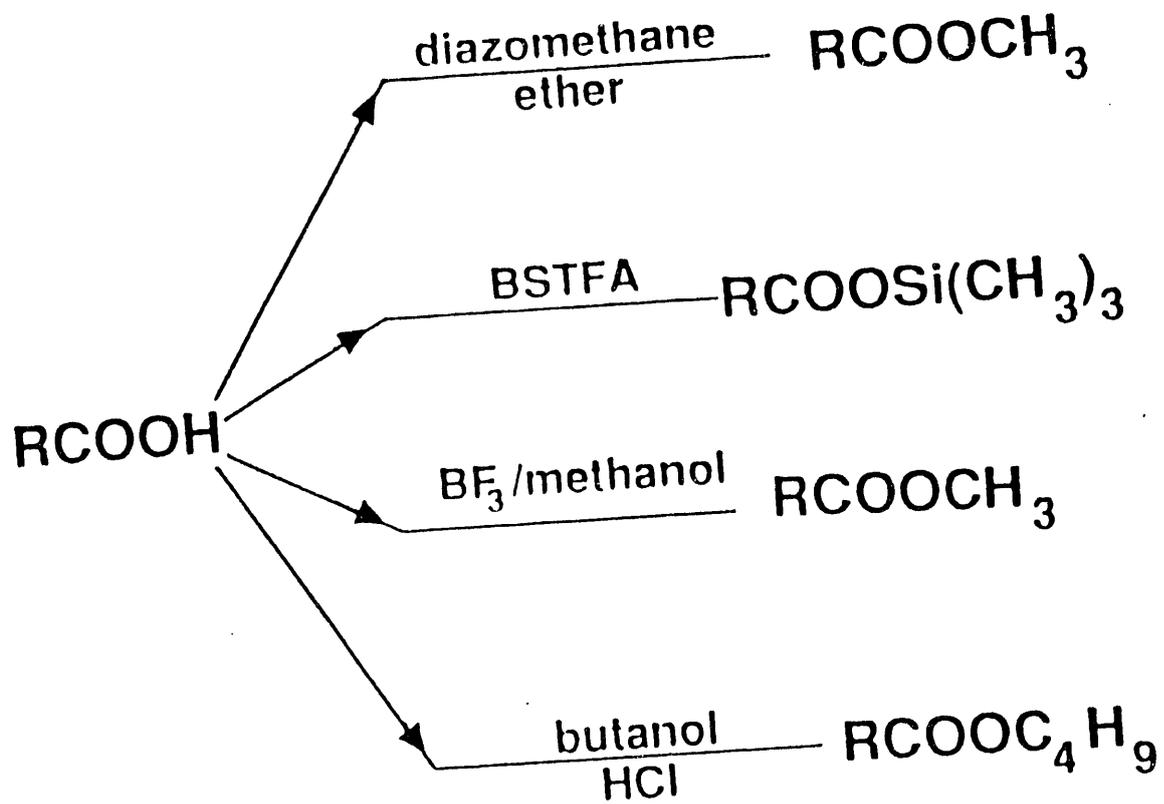
METHODS OF ANALYSIS FOR CHELATORS

- DERIVATIZATION GC/MS
- LC
- LC/MS
- ELECTROSPRAY/MS

DERIVATIZATION GC/MS

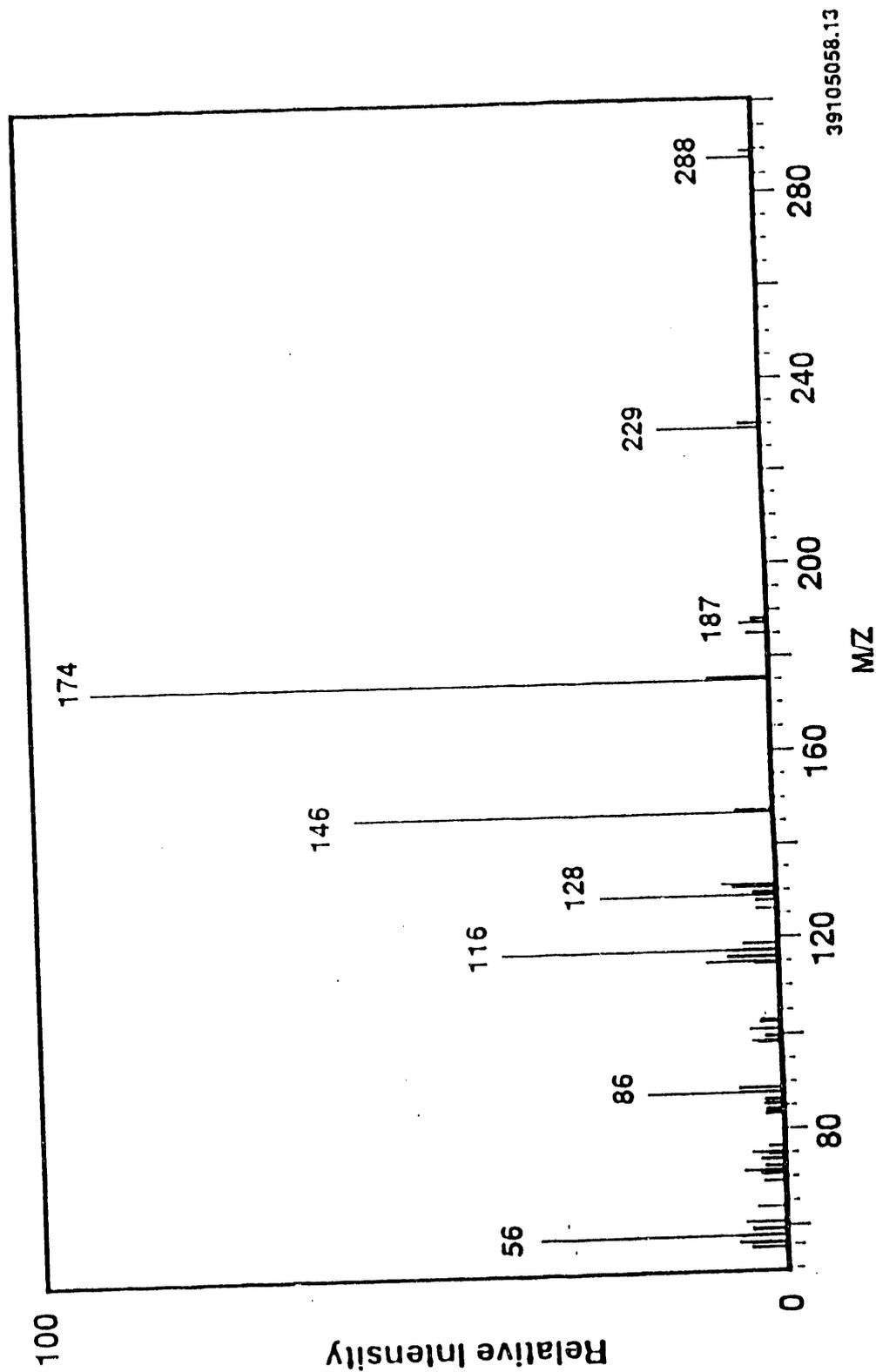
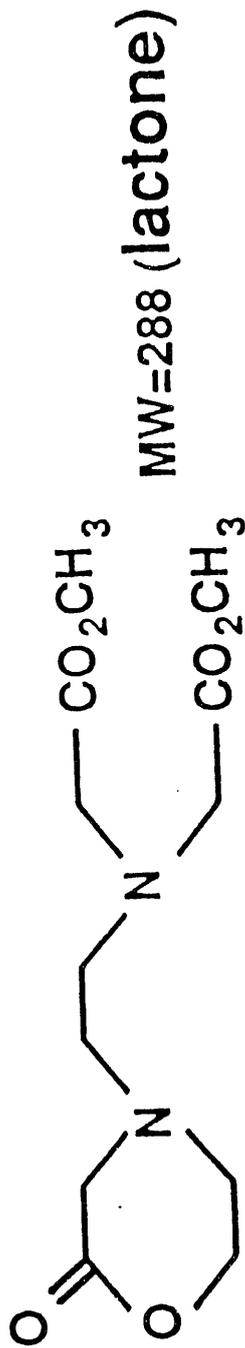
- BORON TRIFLUORIDE/METHANOL
- SILYLATION
- DIAZOMETHANE
- BUTANOL/HCL
- CHLOROETHANOL/HCL

DERIVATIZATION METHODS



REACTION WITH BF₃/METHANOL

Mass Spectrum of Derivatized HEDTA



CONCLUSIONS

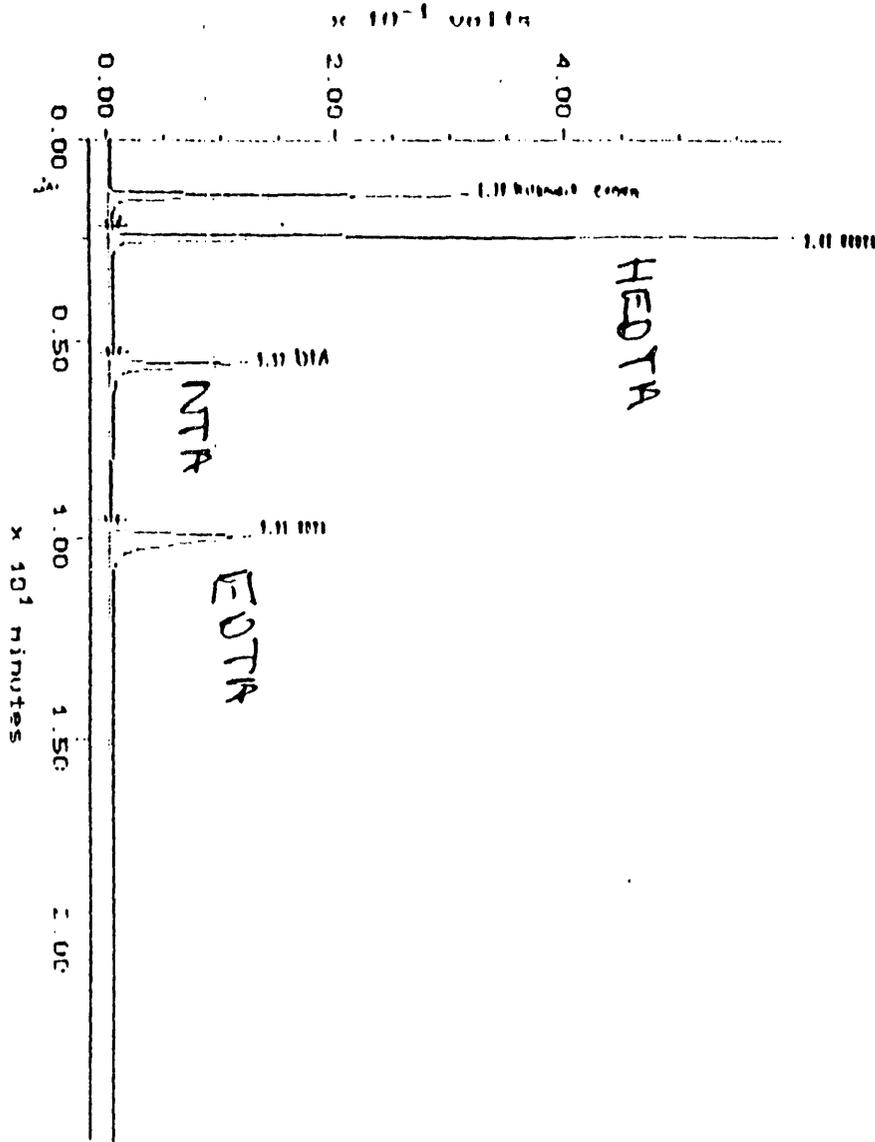
- DIAZOMETHANE-LONG REACTION TIME, MULTIPLY METHYLATED PRODUCTS
- SILYLATION-PARENT ION TYPICALLY FRAGMENTS SEVERLY
- **BF₃/METHANOL-METHYLATE AT CARBOXYLIC ACID SITES, LACTAM & LACTONE FORMATION, BEST REACTION**
- BUTANOL/HCL-FORMS BUTYL ESTERS, SLIGHTLY HIGHER FID RESPONSE THAN METHYL ESTERS
- CHLOROETHYL ESTERS-HIGH ECD RESPONSE, FAIRLY LOW YIELDS

DISADVANTAGES OF DERIVATIZATION

- MAY REQUIRE ADDITIONAL SAMPLING HANDLING
- MAY GIVE LOW OR VARIABLE RECOVERIES
- OFTEN REQUIRES THE USE OF HAZARDOUS REAGENTS
- DOESN'T ALLOW TO ANALYZE AQUEOUS PHASE-ONLY DERIVATIZABLE AND EXTRACTABLE

HPLC

- W.R. GRACE METHOD
- CU OR FE
- OUR METHOD HAS NO CU IN MOBILE PHASE



0078 (6/16/91) Dynamic Solution, Division of Millipore

MAXIMA 620 PEAK INTEGRATION REPORT

Acquired: 16-JUN-1991 14:41:00

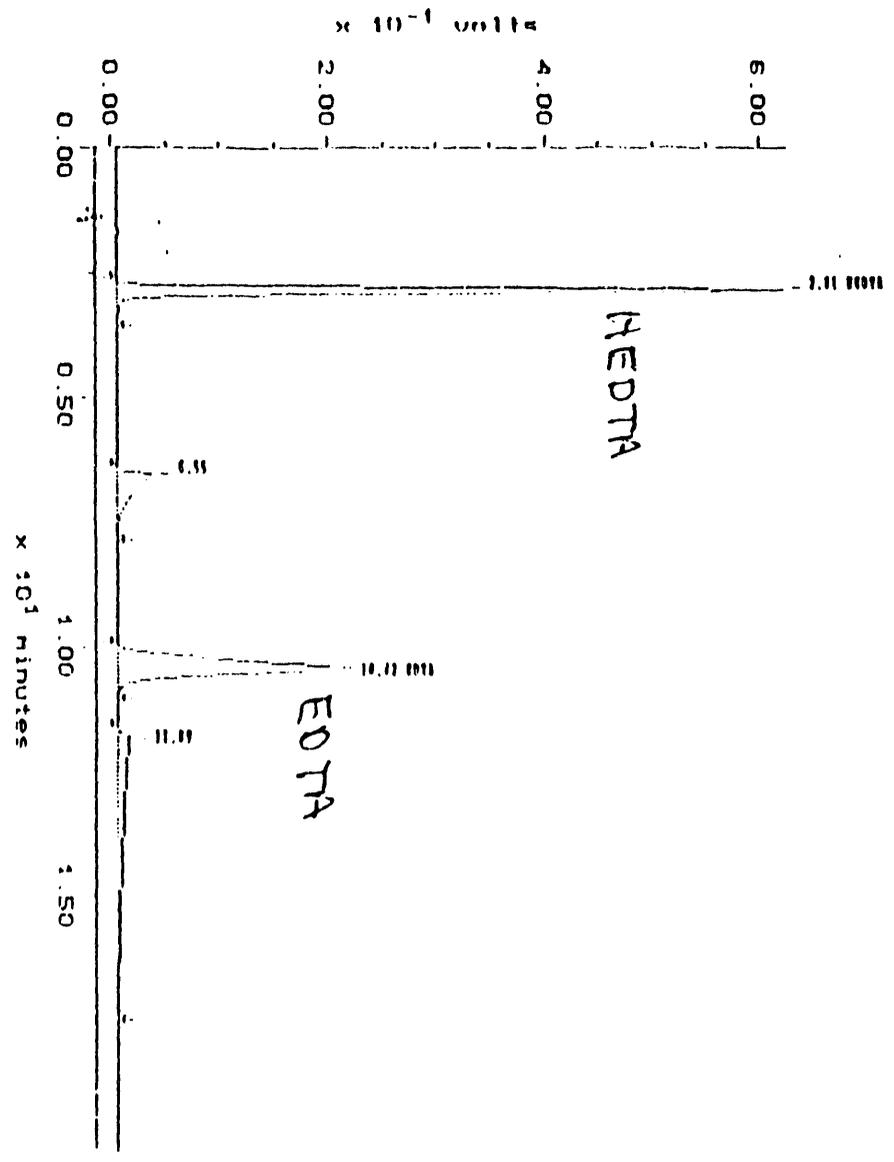
SAMPLE: 0078-00078-0078

In Method: Grace method
 Acquired: 16 JUN 1991 14:41
 Rate: 2.0 gallons/week
 Duration: 25.320 minutes
 Operator:

Type: 0078
 Instrument: Waters 620C
 File Name: 01-16-9
 Inj Vol: 20.0
 Injection Volume: 20.0

DETECTOR: Model 110

PK#	TR	Peak Start (minutes)	Peak End (minutes)	Retention (minutes)	Type	Peak Area (intensity*sec)	Peak Weight (intensity)	Area Percent	Height Percent	Component Name
1	1	0.255	0.267	0.262	DP	2001700.0	200207.10	17.10	27.10	MAXIMA 620C
2	1	0.267	0.267	0.258	DP	2001267.0	200099.02	16.10	23.20	0078
3	2	0.267	0.255	0.267	DP	1023095.7	100299.52	11.97	9.50	NTA
4	2	0.255	0.267	0.260	DP	1591507.5	100007.20	10.10	9.50	0078
TOTALS:						11000150	1000000.0			



SYNTHETIC URINE

VETRA (c)1987 Dynamic Solutions, Division of Millipore

MAXIMA 820 PEAK INTEGRATION REPORT

Related: 15 MAR 1991 16:30:36

SAMPLE: 010 00 3/12 00
 Inj Method: 007000; 007000
 Acquired: 15 MAR 1991 16:00
 Rate: 2.0 µl/min/sec
 Duration: 20.000 minutes
 Operator:

Type: 0000
 Instrument: VETRA 820C
 Filtration: 01-01-0
 Inlet: 0
 Injection Volume: 20.0

DETECTOR: Model 440

PK#	ID#	Peak Start (minutes)	Peak End (minutes)	Retention (minutes)	Type	Peak Area (microvolts-sec)	Peak Height (microvolts)	Area Percent	Height Percent	Component Name
1	1	0.550	0.550	0.550	00	000000.0	00000.00	00.00	00.00	EDTMA
2		0.550	0.550	0.550	00	000000.0	00000.00	00.00	00.00	EDTMA
3	3	10.000	10.000	10.000	00	000000.0	00000.00	00.00	00.00	EDTA
4		11.000	11.000	11.000	00	000000.0	00000.00	00.00	00.00	HEDTA
TOTAL						000000.0	00000.00			

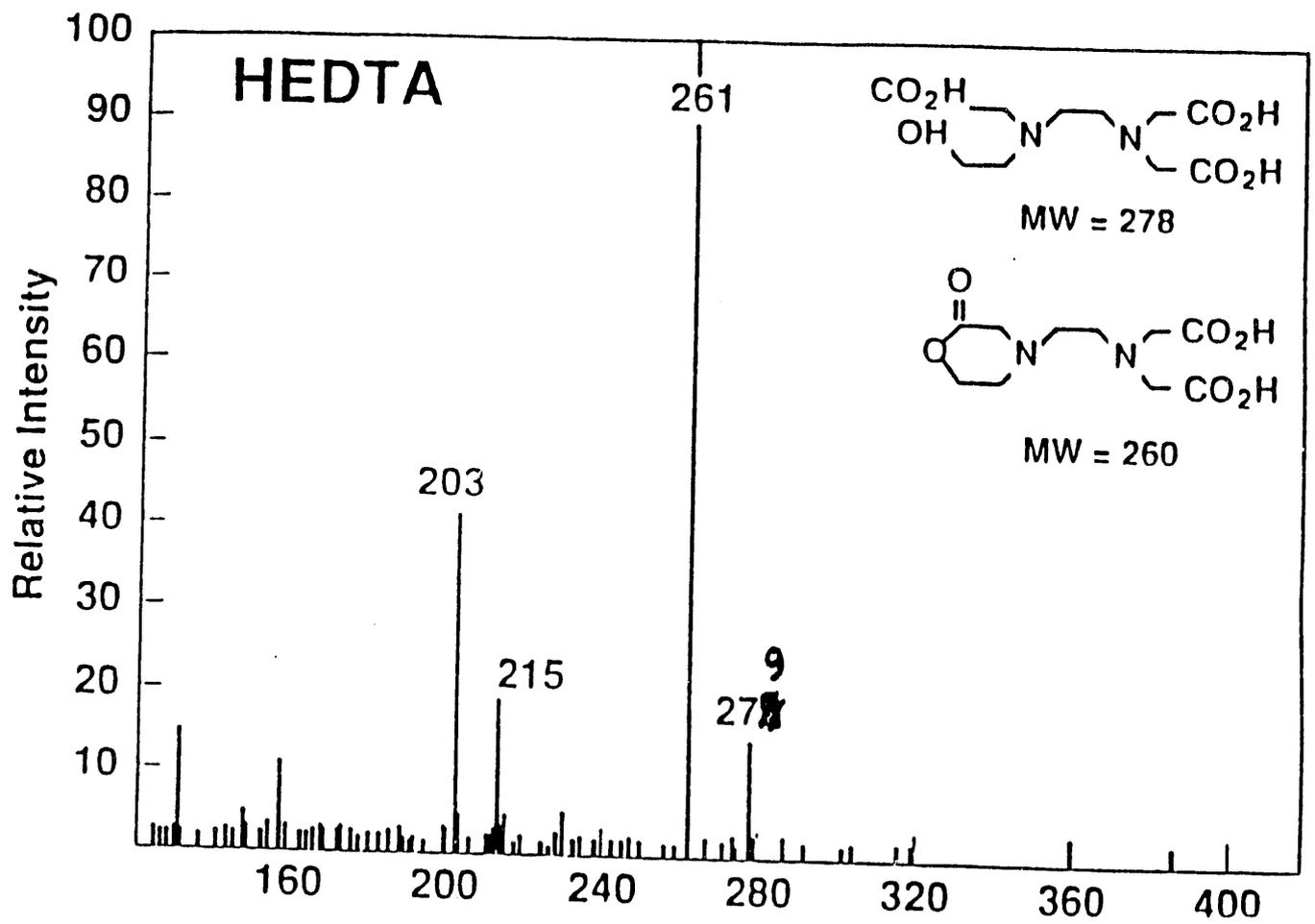
CLEANUP PROCEDURE FOR SYNTHETIC WASTE

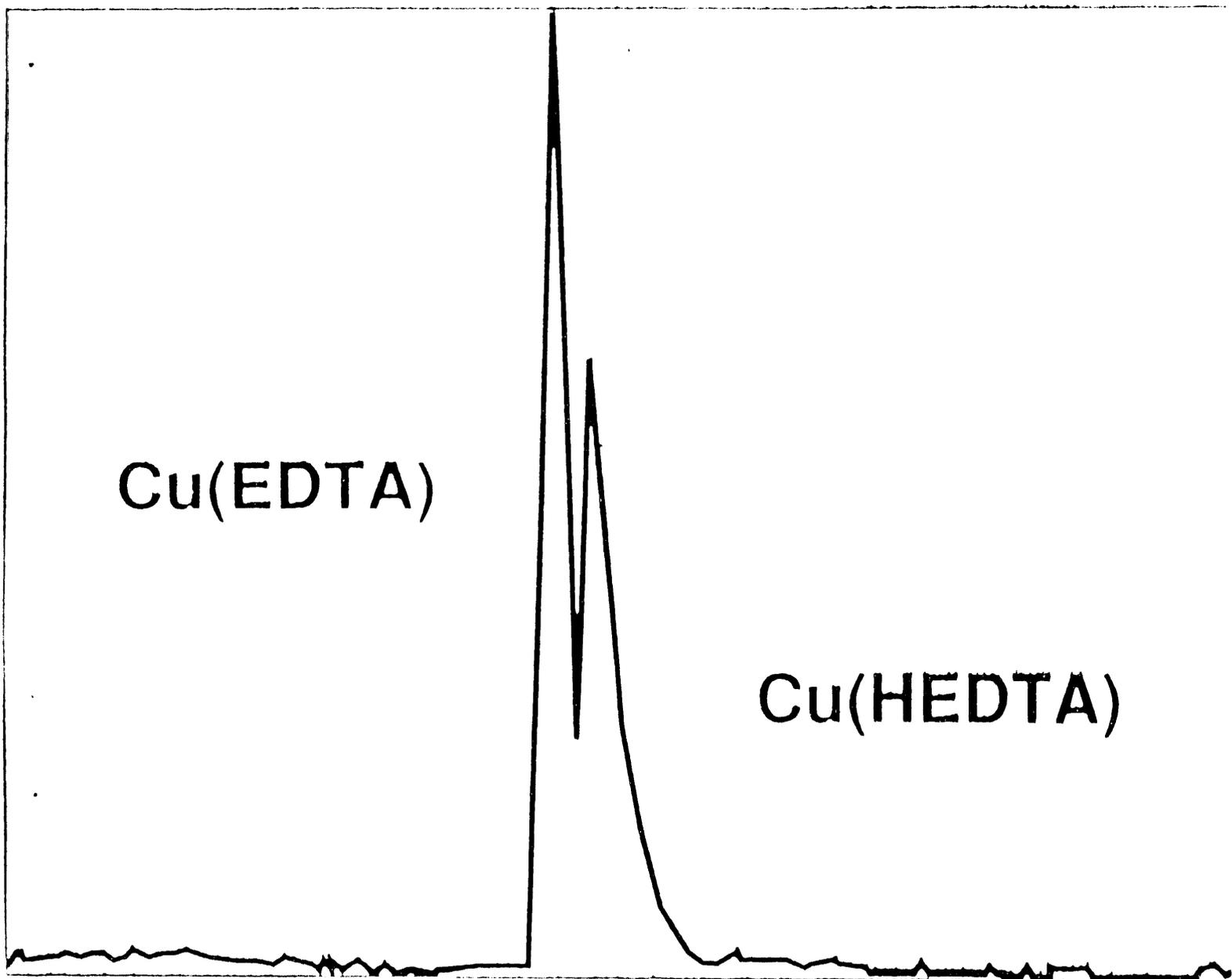
- GOING FROM STANDARDS TO SIMULATED WASTES PRODUCED.CLEANUP CHALLENGE BEFORE ANALYSIS
- NEED TO REMOVE CONTAMINANTS
- METHOD INVOLVES ADDITION OF COPPER SULFATE, ACID PRECIPITATION, CENTRIFUGATION , PH ADJUST TO 6.5

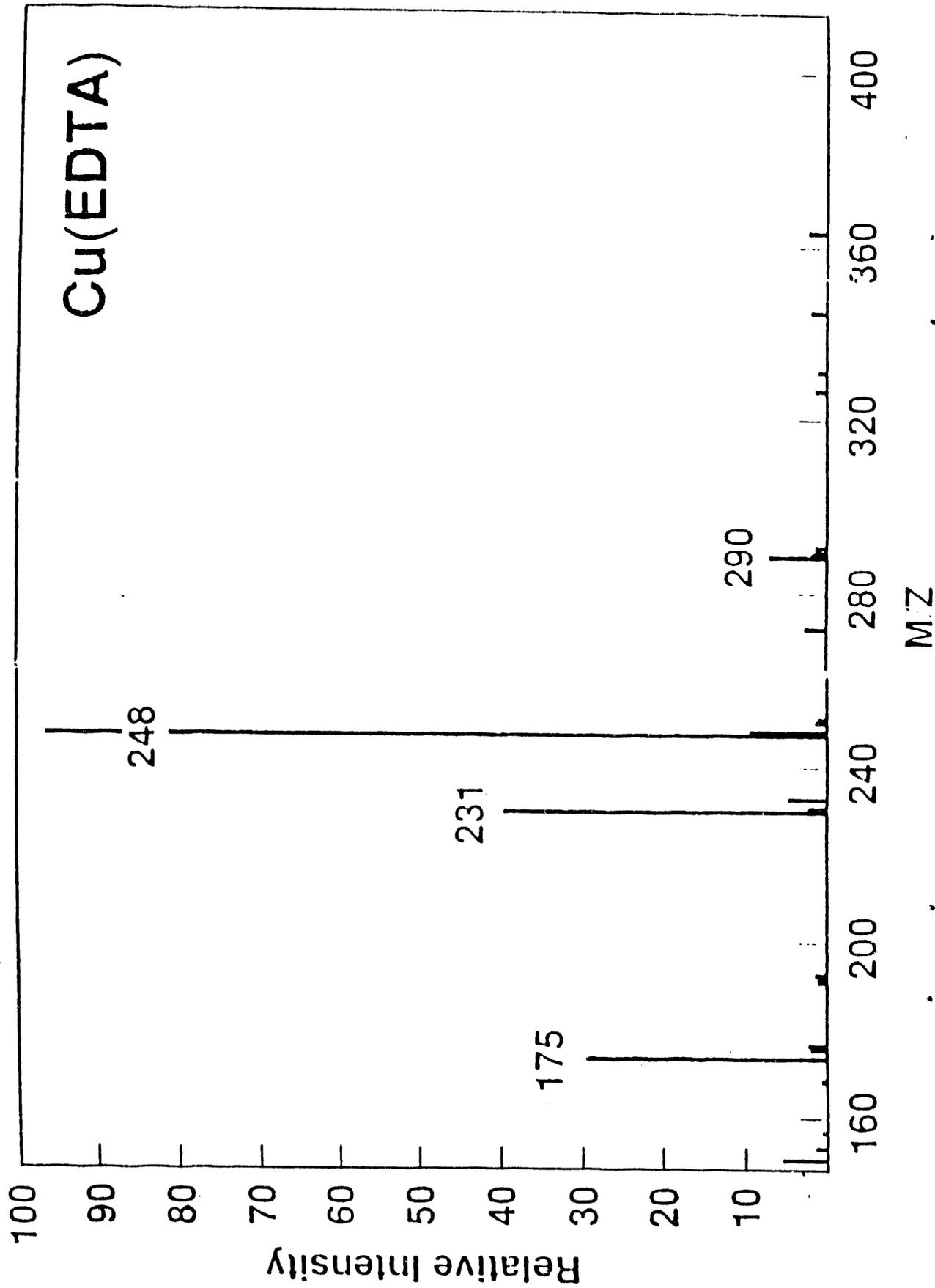
LC/MS

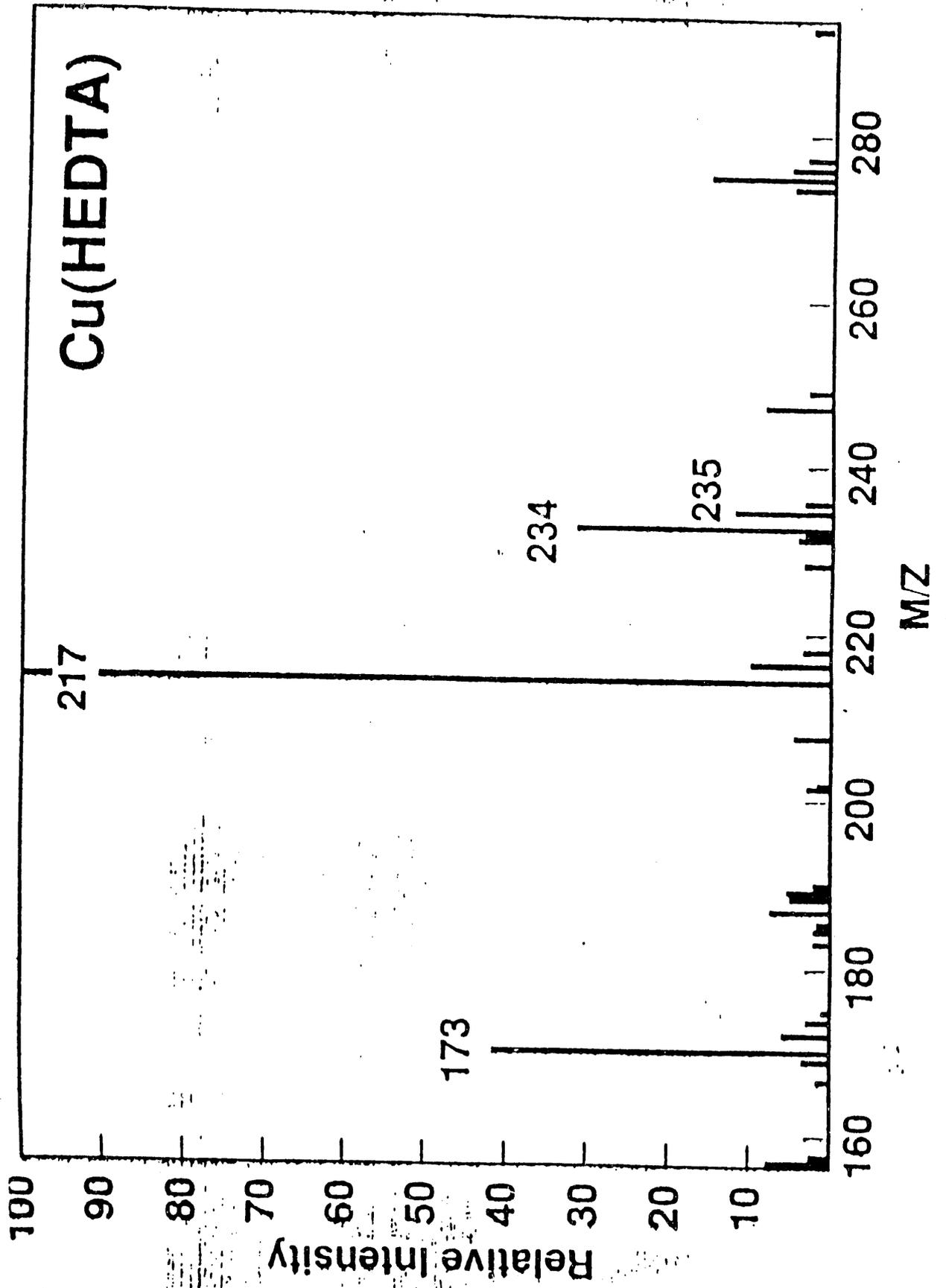
- MOBILE PHASES COMPATIBLE WITH LC NOT FOR MS
- REVERSE PHASE C2 LICHROSORB COLUMN
- PARTICLE-BEAM VS. THERMOSPRAY INTERFACES
- RESULTS PROVIDE EXTENSION TO LC/MS-ICP/MS

THERMOSPRAY LC/MS OF HEDTA

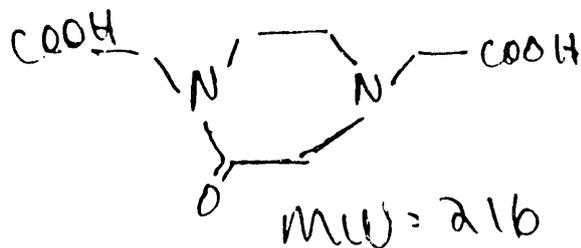
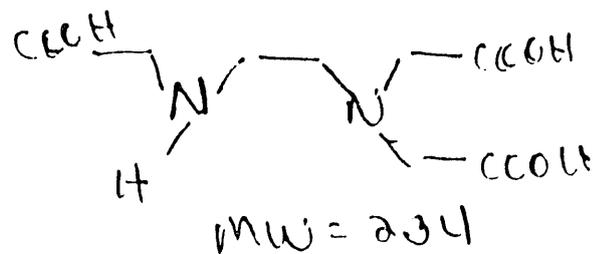
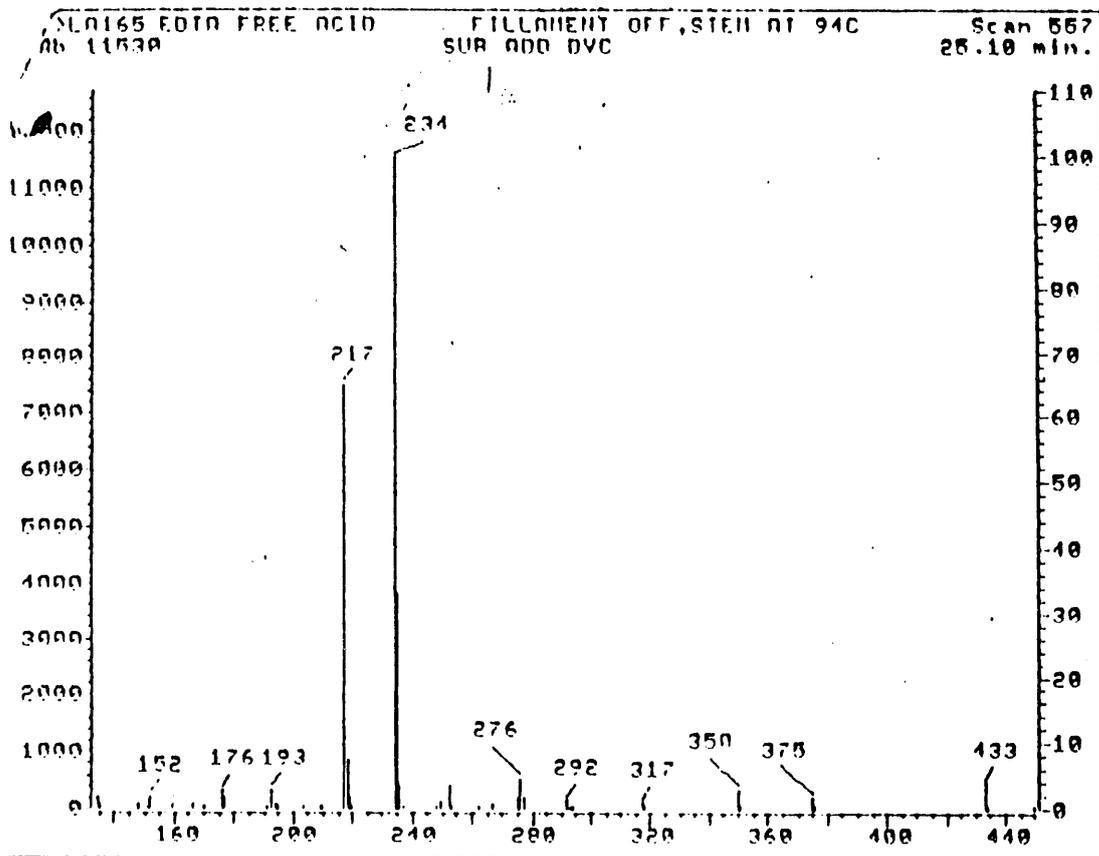




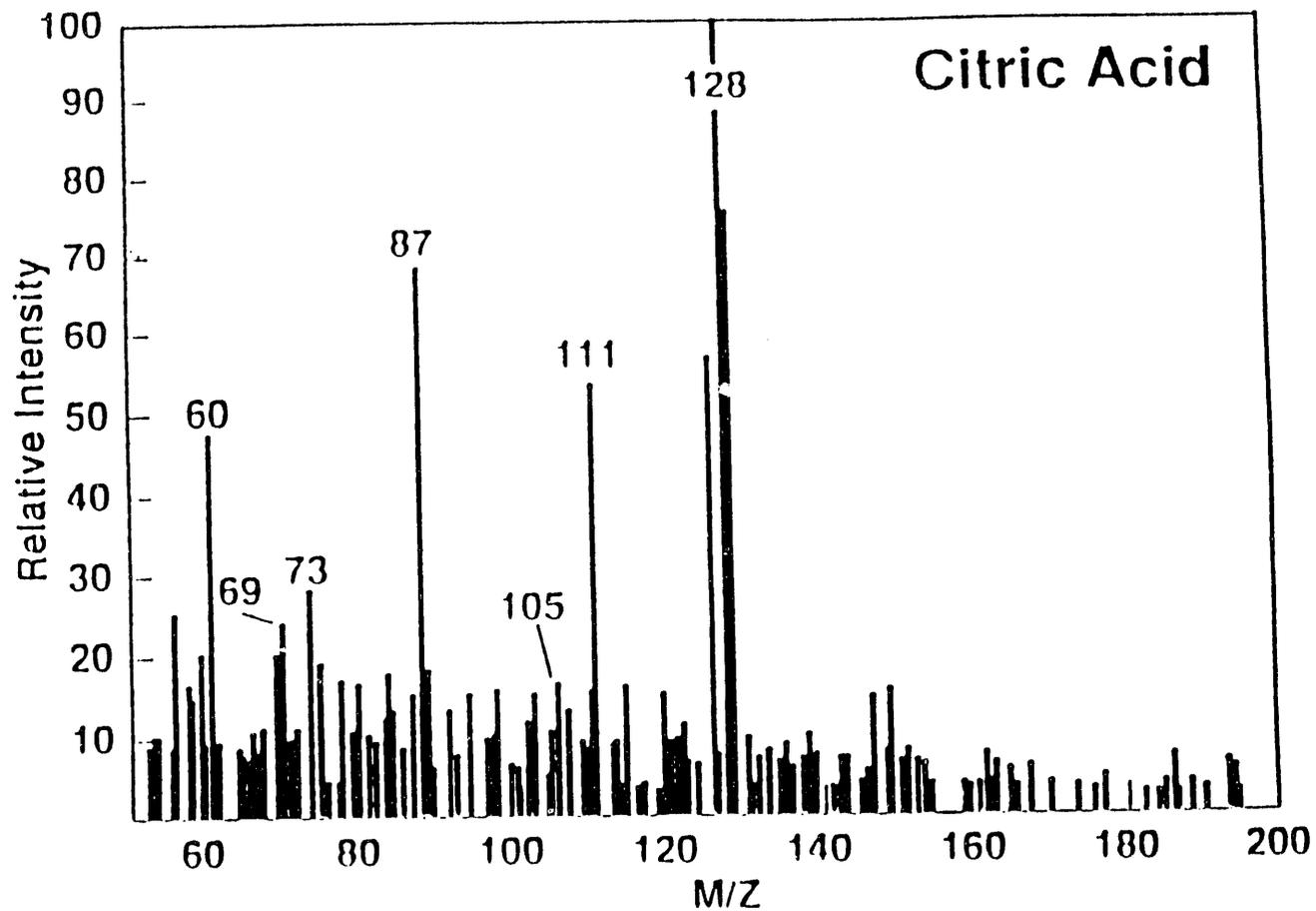




THERMOSPRAY LC/MS OF ED3A



PARTICLE-BEAM LC/MS



CONCLUSIONS

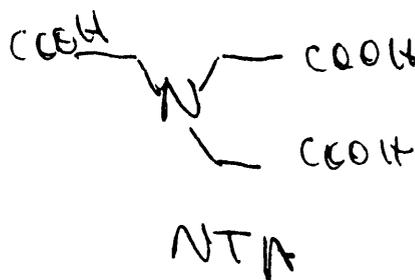
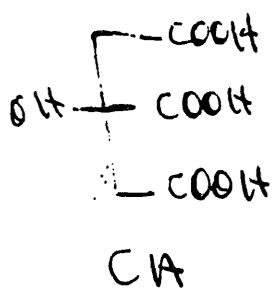
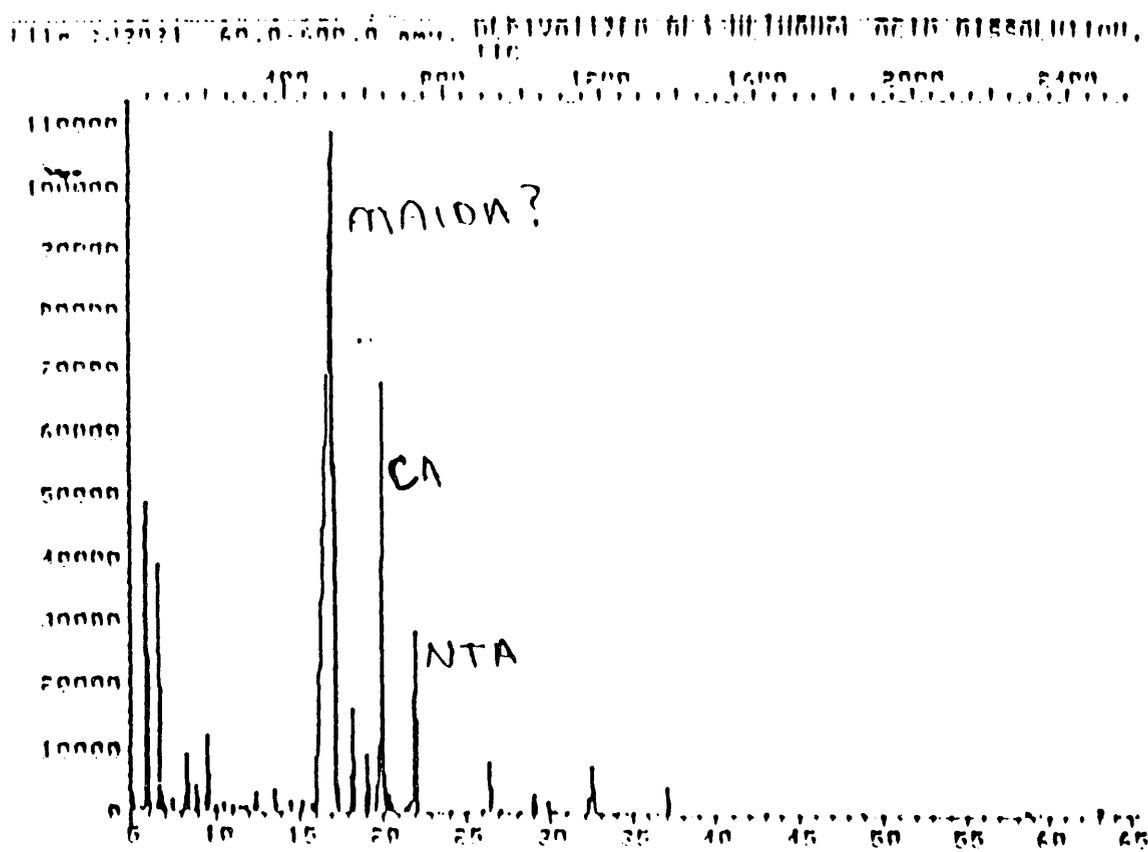
- Particle-Beam LC/MS Provides Extensive Fragmentation. Difficult to Unambiguously Identify
- Mass Spectra Obtained from Free Acids Different than Complexed
- Thermospray LC/MS Can be Used for Identification of Chelators and Chelator Fragments
- LC/MS Coupled to ICP/MS will Allow Organic and Metal to be Identified Simultaneously

ANALYSIS OF TANK 101-SY CORE SAMPLES

**ADVANCED ORGANIC ANALYTICAL METHODS
GROUP**

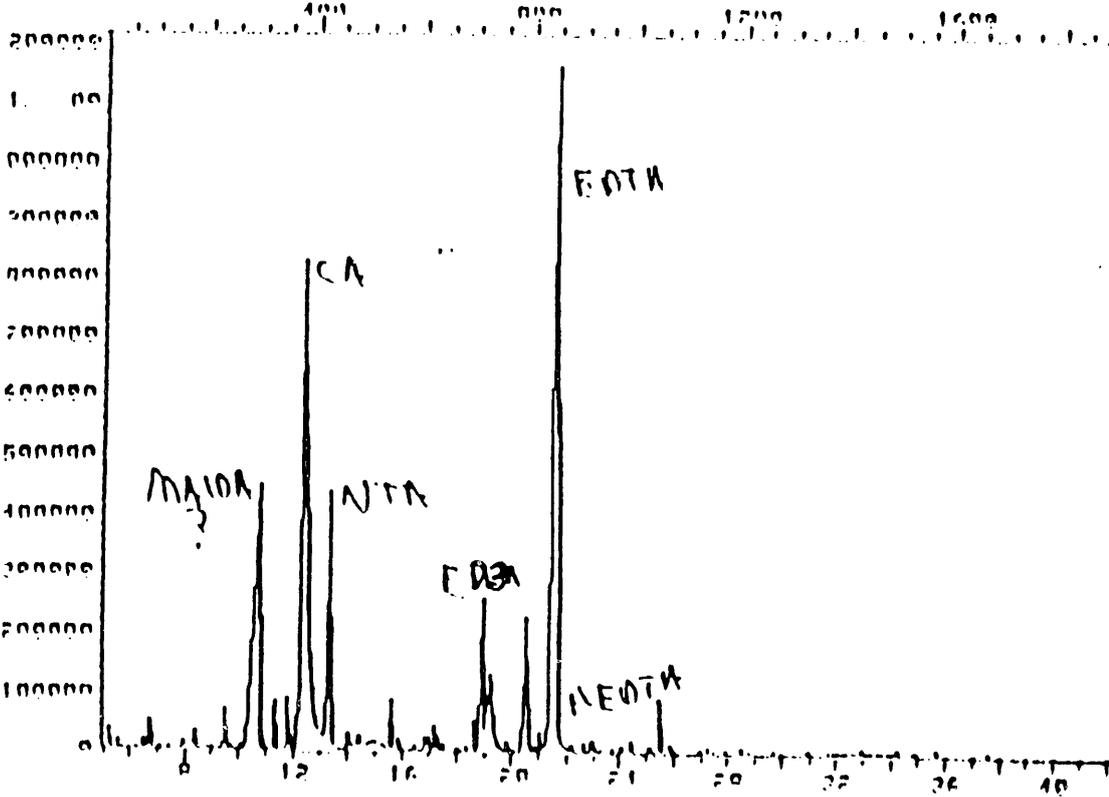
DR. J.A. CAMPBELL, PRINCIPAL INVESTIGATOR

ACID DISSOLUTION FOLLOWED BY DERIVATIZATION

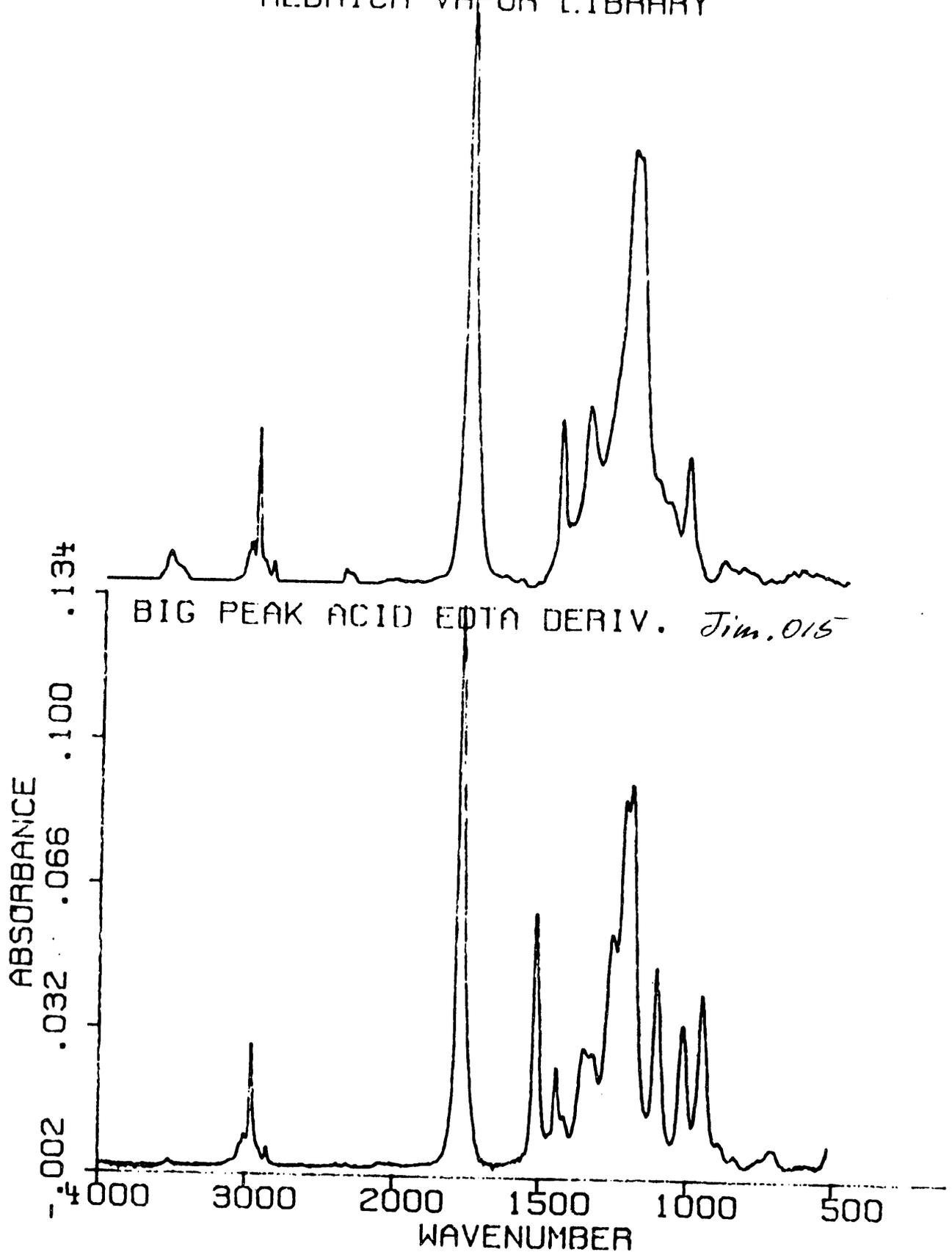


WATER EXTRACT OF SOLID DERIVATIZED

110 3.00251 50.0 5000.0 500. 101-5V. 712. WATER EXTRACT, DERIVATIZED 110



LIBRARY SEARCH RESULT FOR PEAK
10.93 MINUTES INTO RUN
OFN = 553
CITRIC ACID, TRIMETHYL ESTER
RTN = 3562
ALDRICH VAPOR LIBRARY



GC ANALYSIS OF ORGANICS IN TANK 107-AN

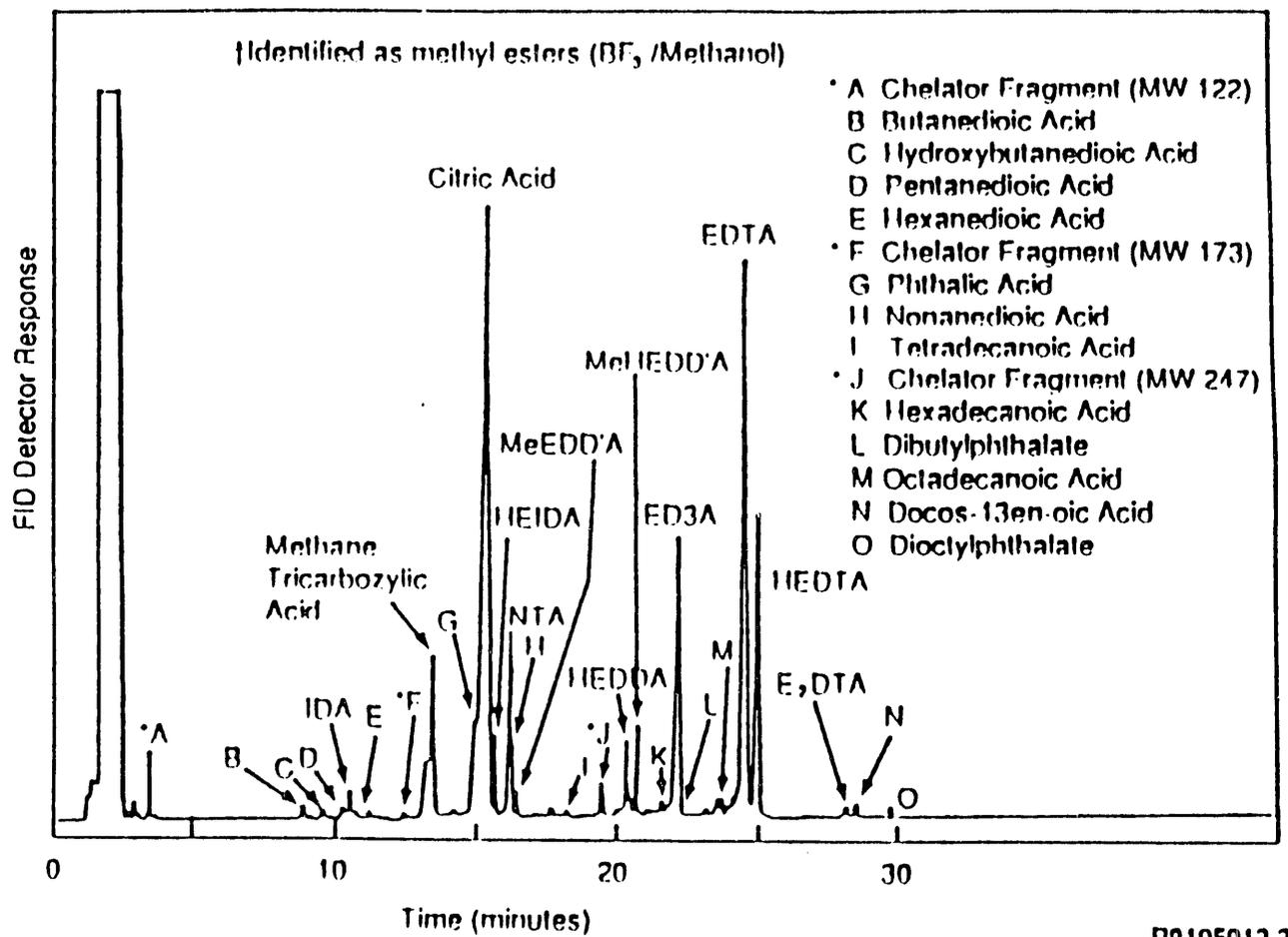


Figure 3.2. GC Analysis of Hydrophilic Organics¹ in Organic Complexant Waste from Tank 107AN

FURTHER STUDIES

- FINISH ANALYZING DATA ON SAMPLE 1
- REPEAT DERIVATIZATION ON SAMPLE 1
- ANALYZE OTHER CORE SAMPLES FOR CHELATORS
- DEVELOP METHODS FOR ISOLATING REMAINING TOC

- DEVELOP OTHER ANALYTICAL TECHNIQUES TO IDENTIFY REMAINING TOC

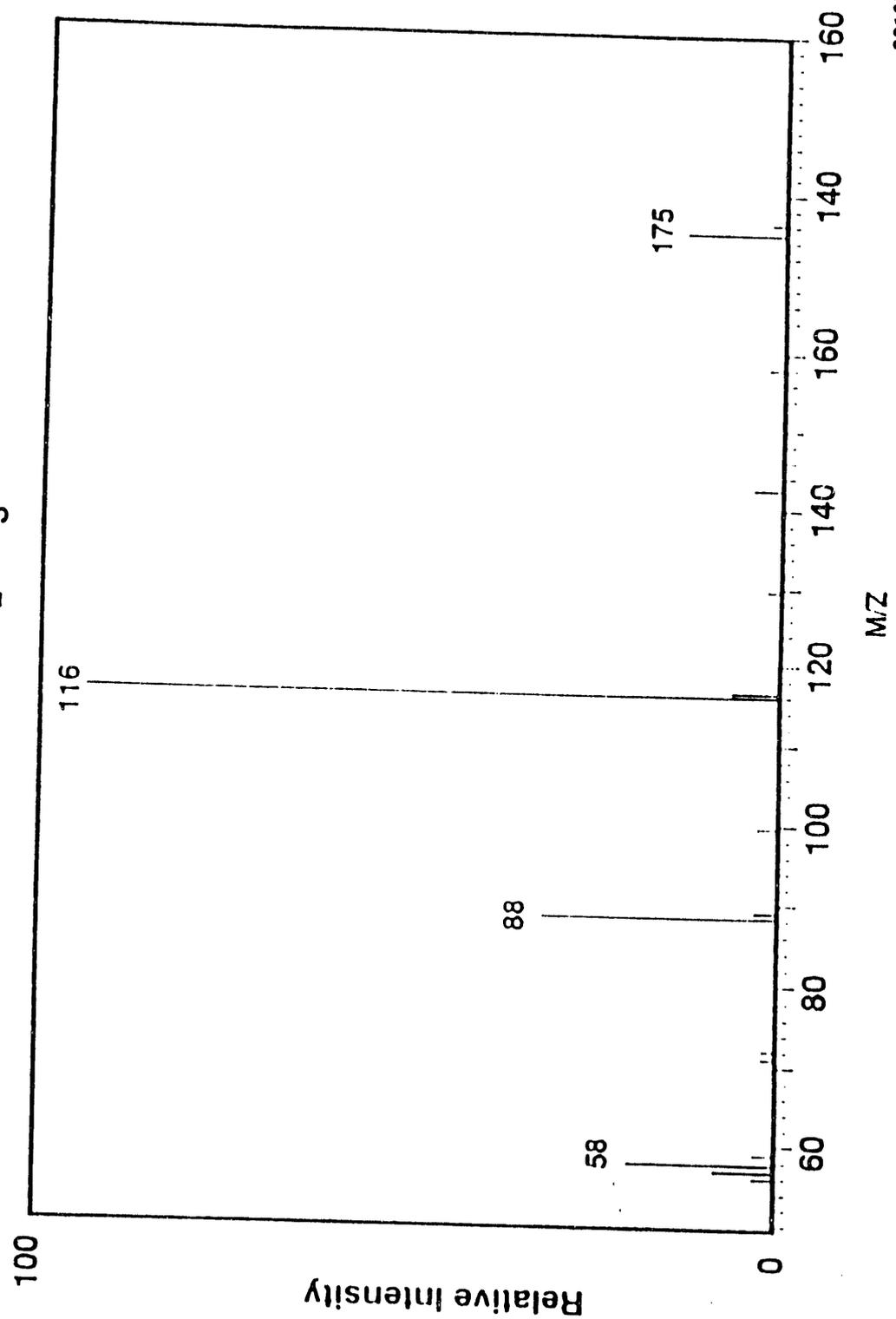
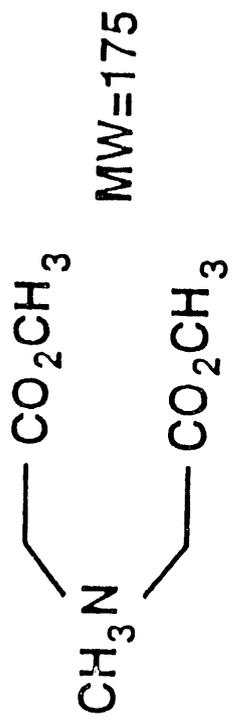
ACKNOWLEDGMENTS

Jim Campbell
Rich Lucke
Scott Clauss
Margaret McCulloch
Roger Bean
Kathy McKeeta
Karen Grant

APPENDIX

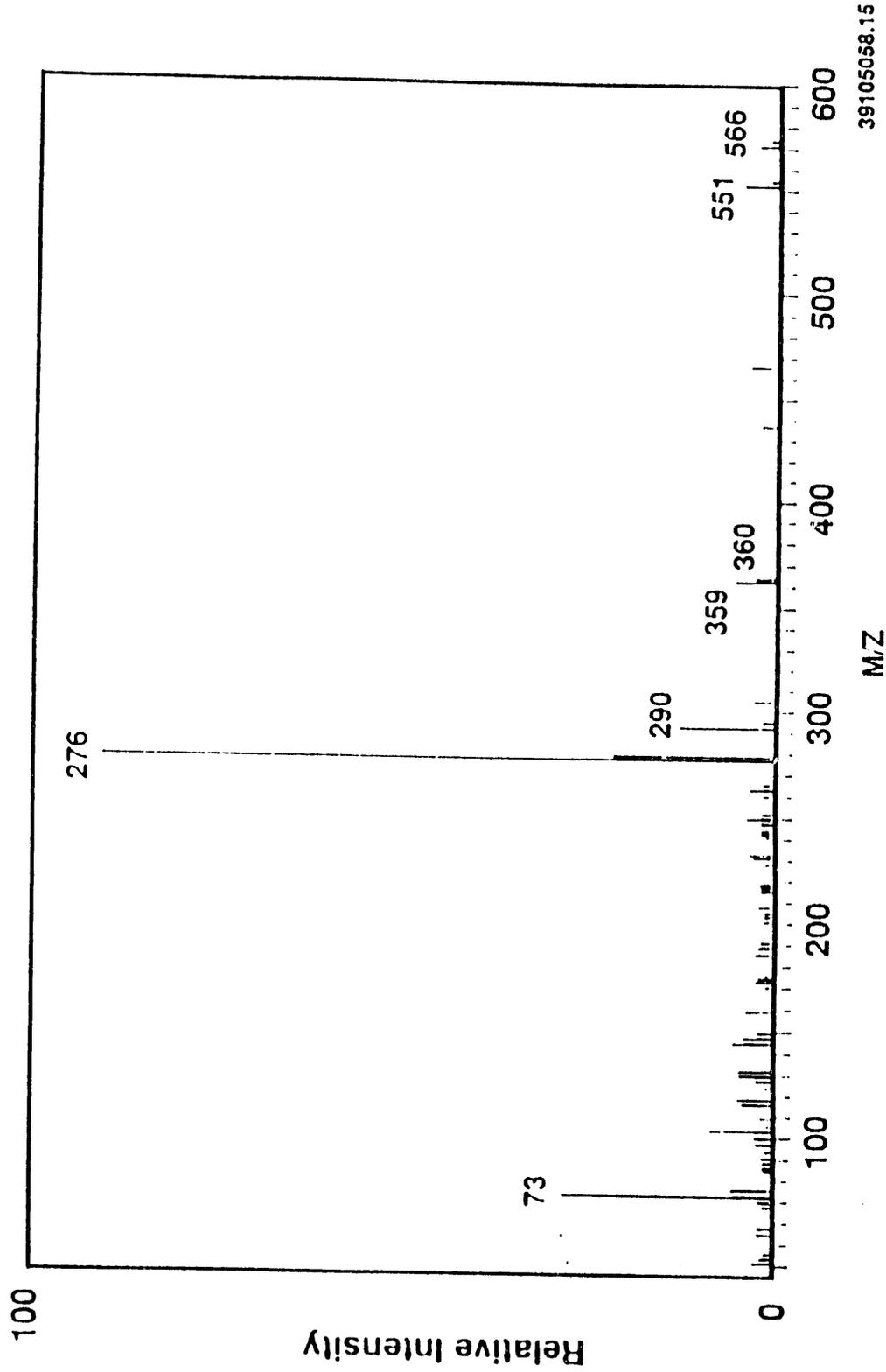
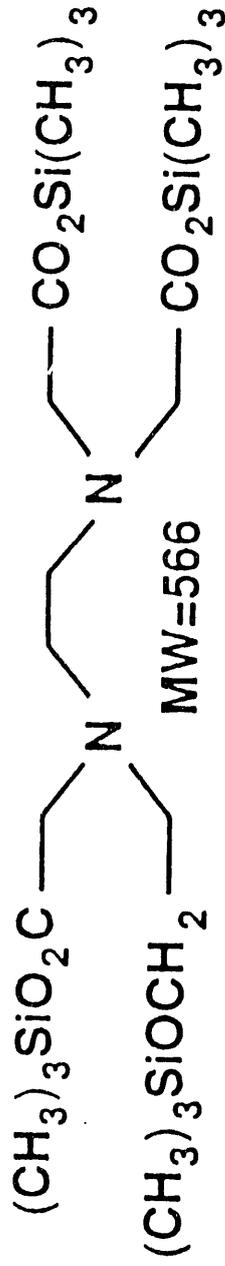
REACTION WITH DIAZOMETHANE

Mass Spectrum of Peak #2



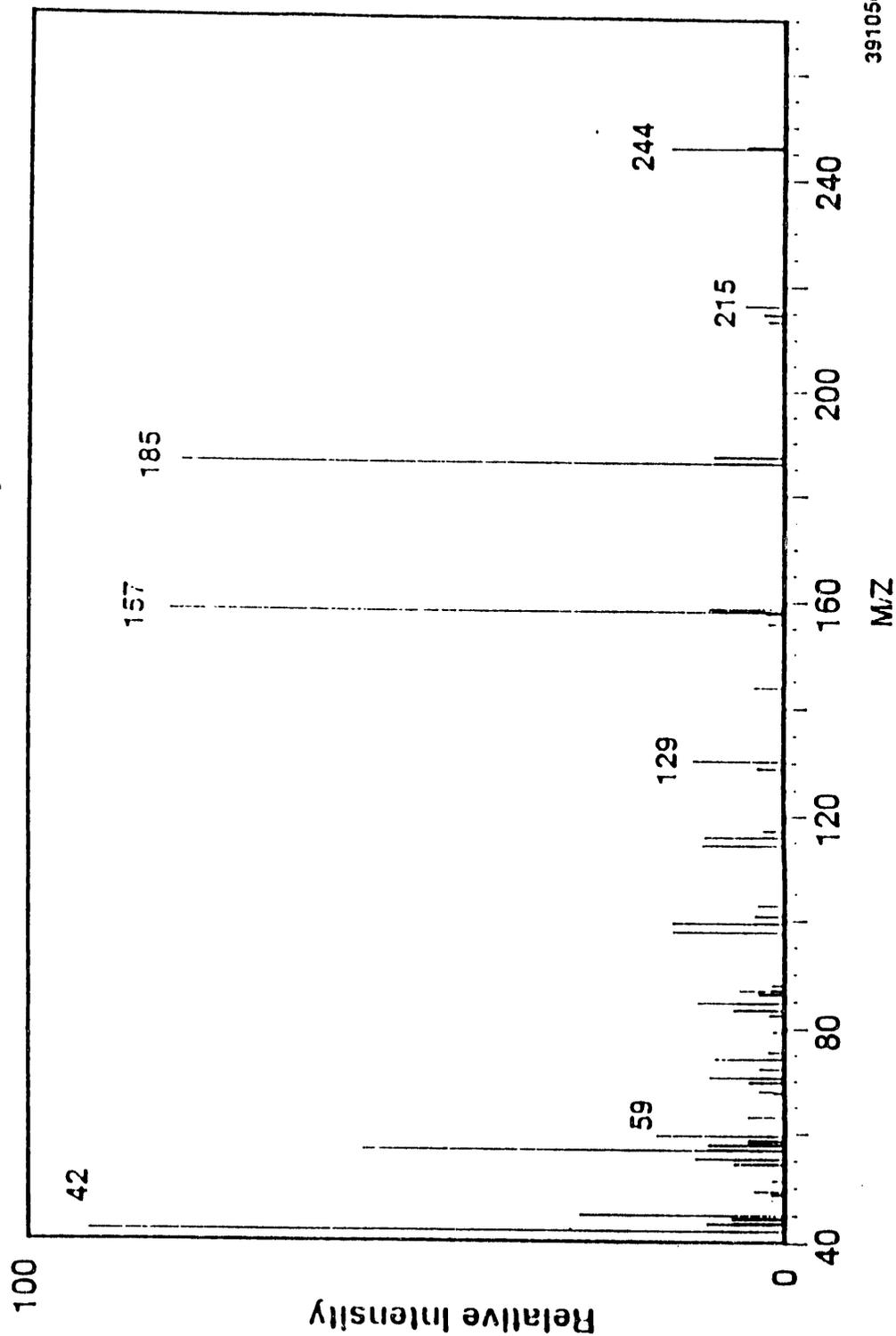
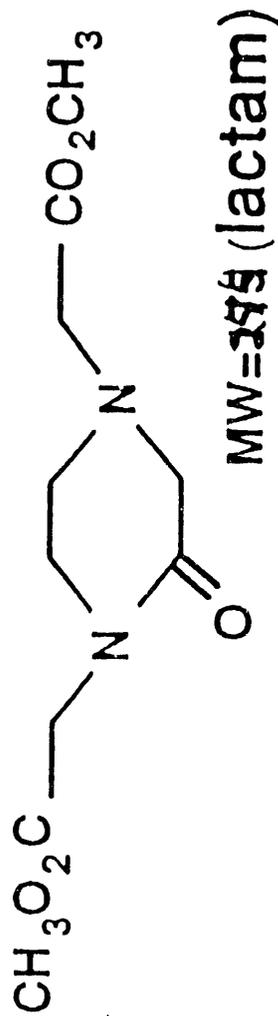
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Mass Spectrum of Derivatized HEDTA



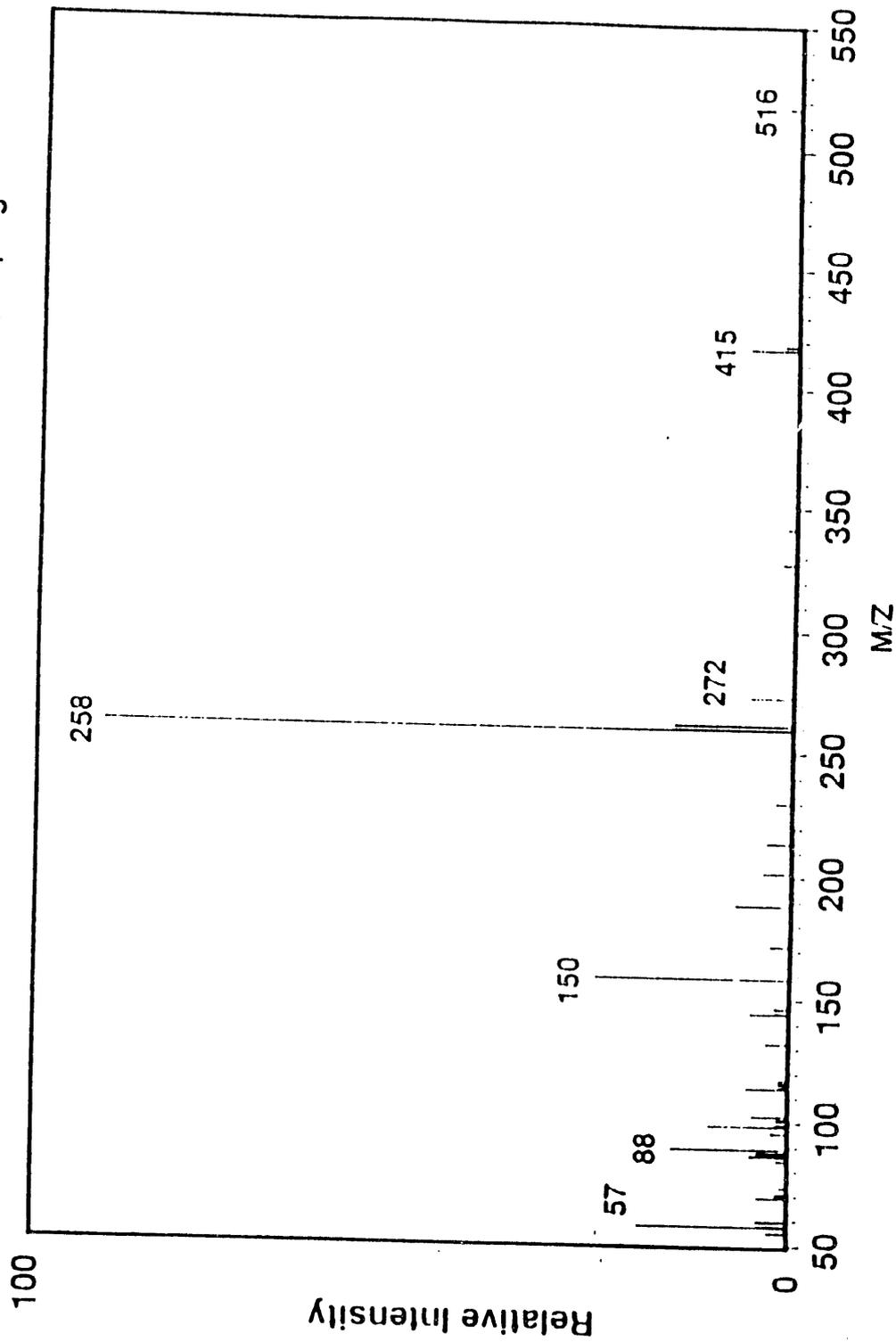
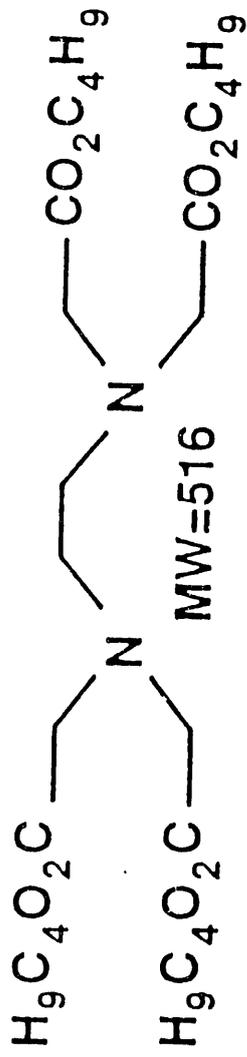
REACTION WITH BF₃/METHANOL

Mass Spectrum of Derivatized ED3A



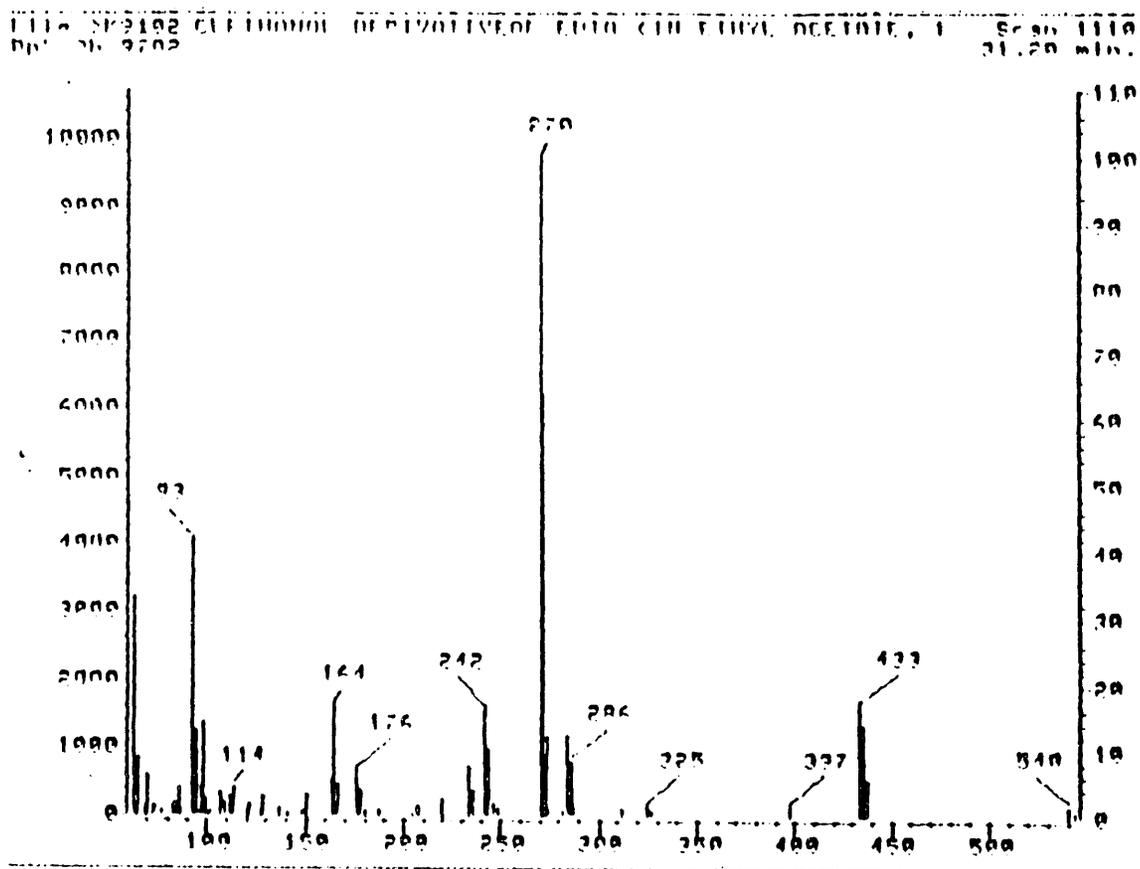
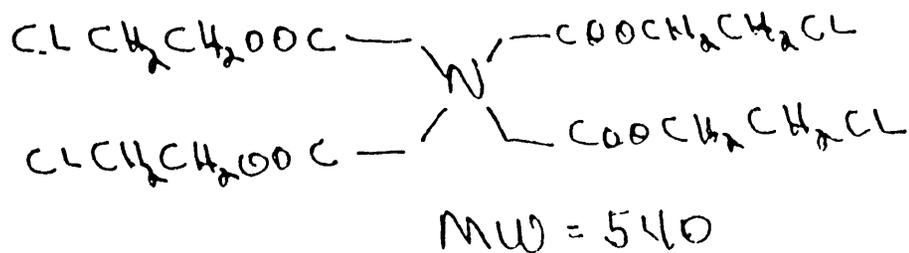
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Mass Spectrum of Derivatized EDTA

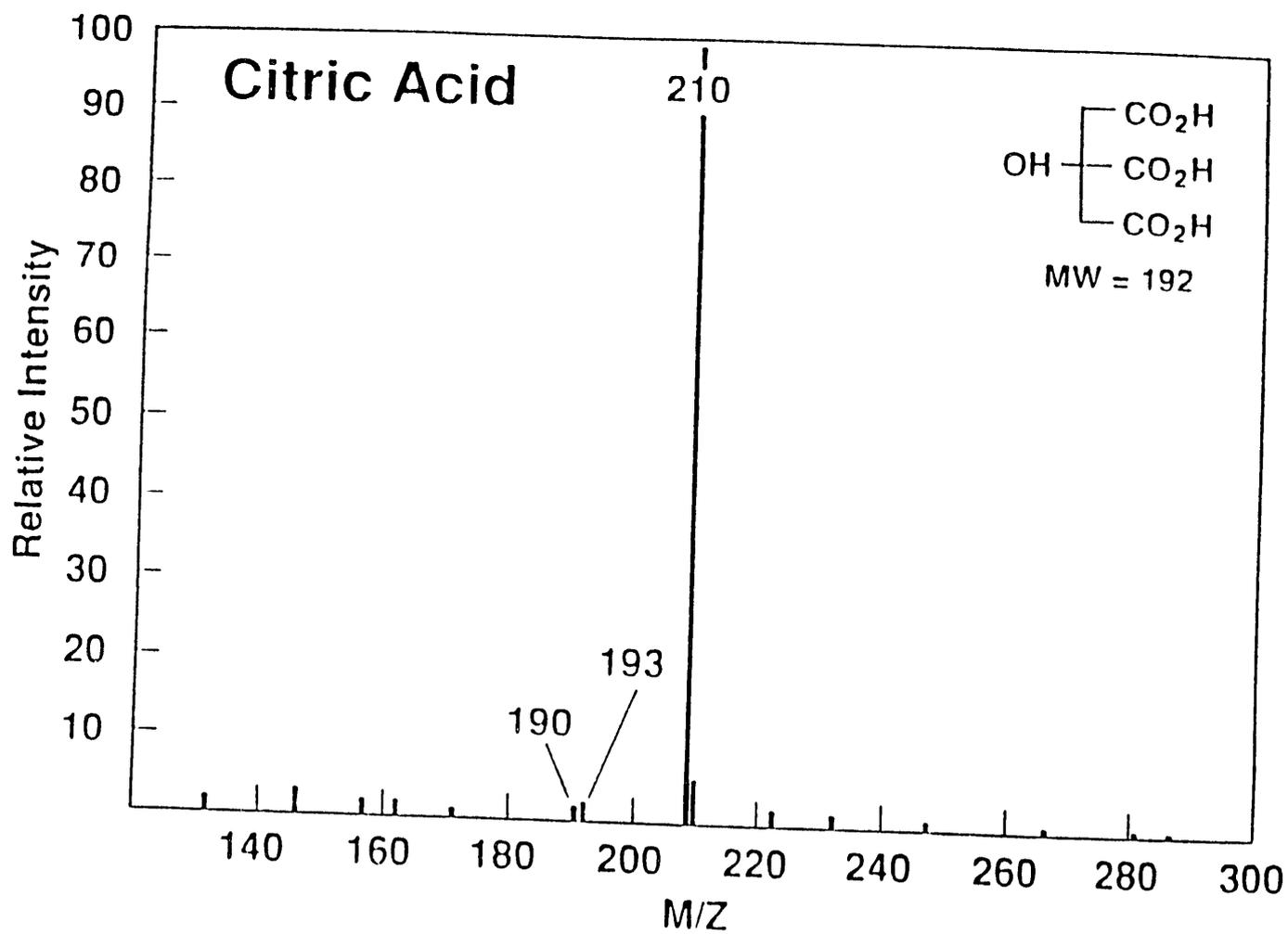


REACTION WITH CHLOROETHANOL/HCL

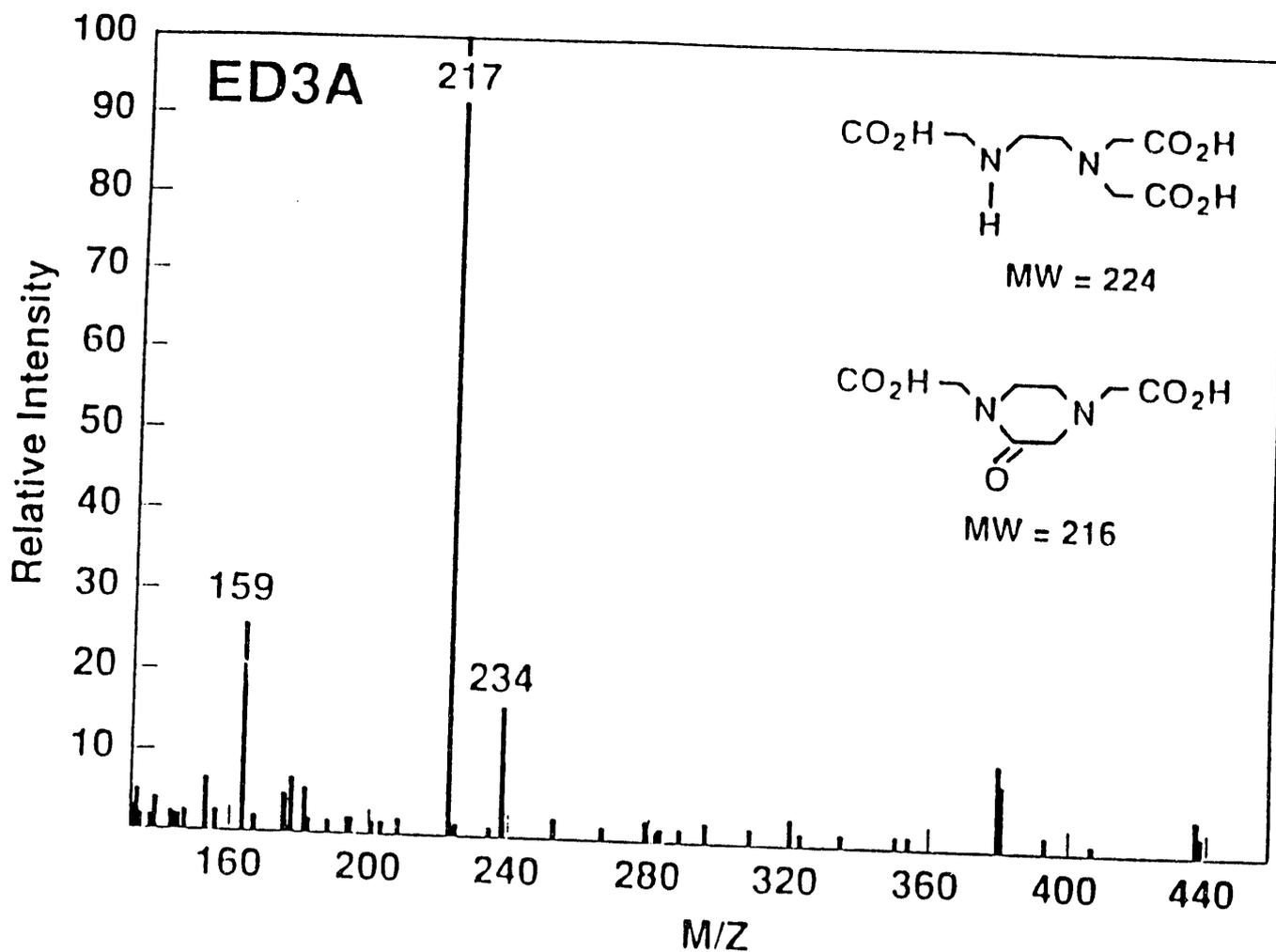
MASS SPECTRUM OF CHLOROETHYL ESTER OF EDTA



THERMOSPRAY LC/MS OF CITRIC ACID

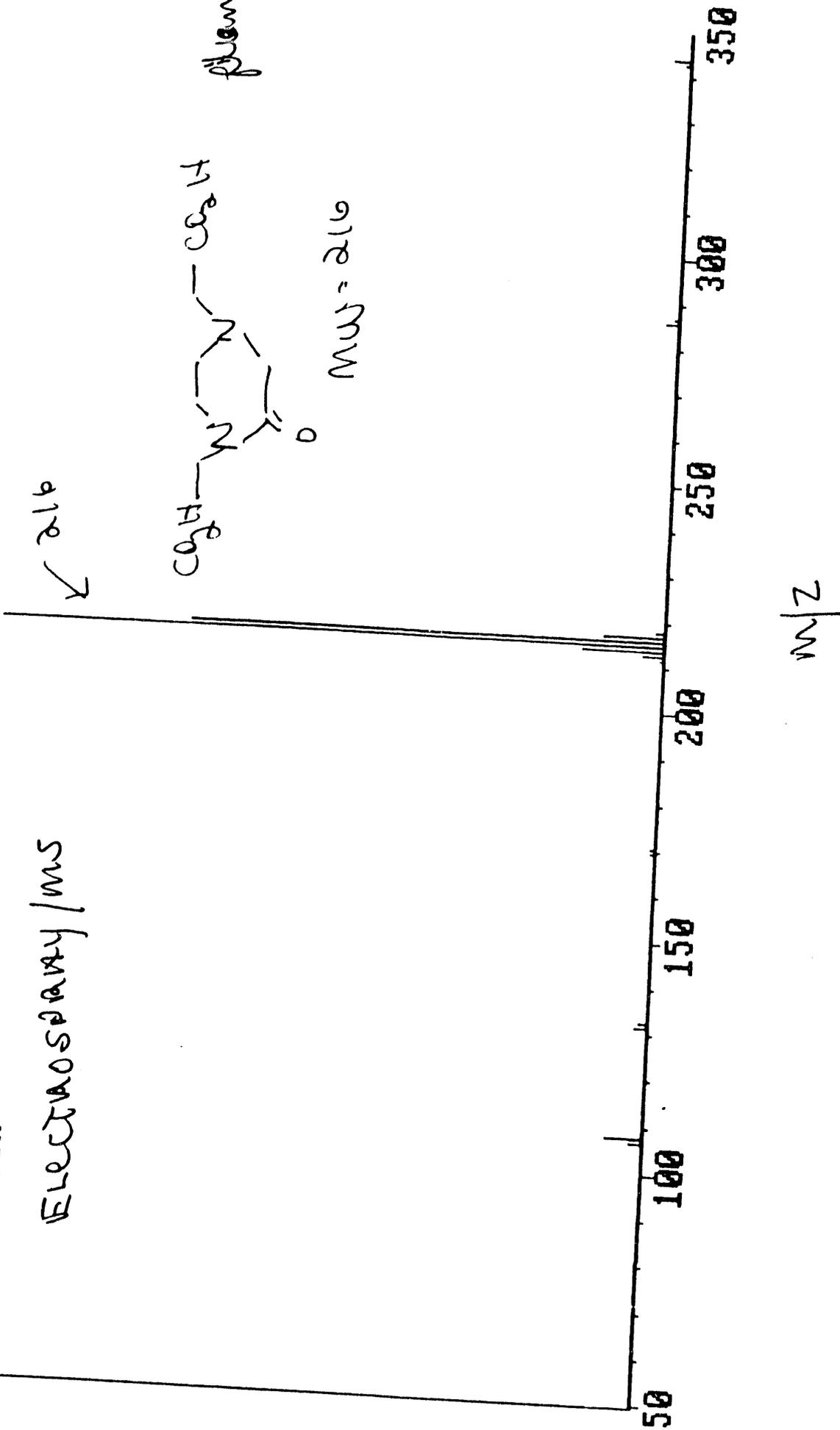


THERMOSPRAY LC/MS OF ED3A



ED3A

ELECTROSPRAY/MS



MW = 216

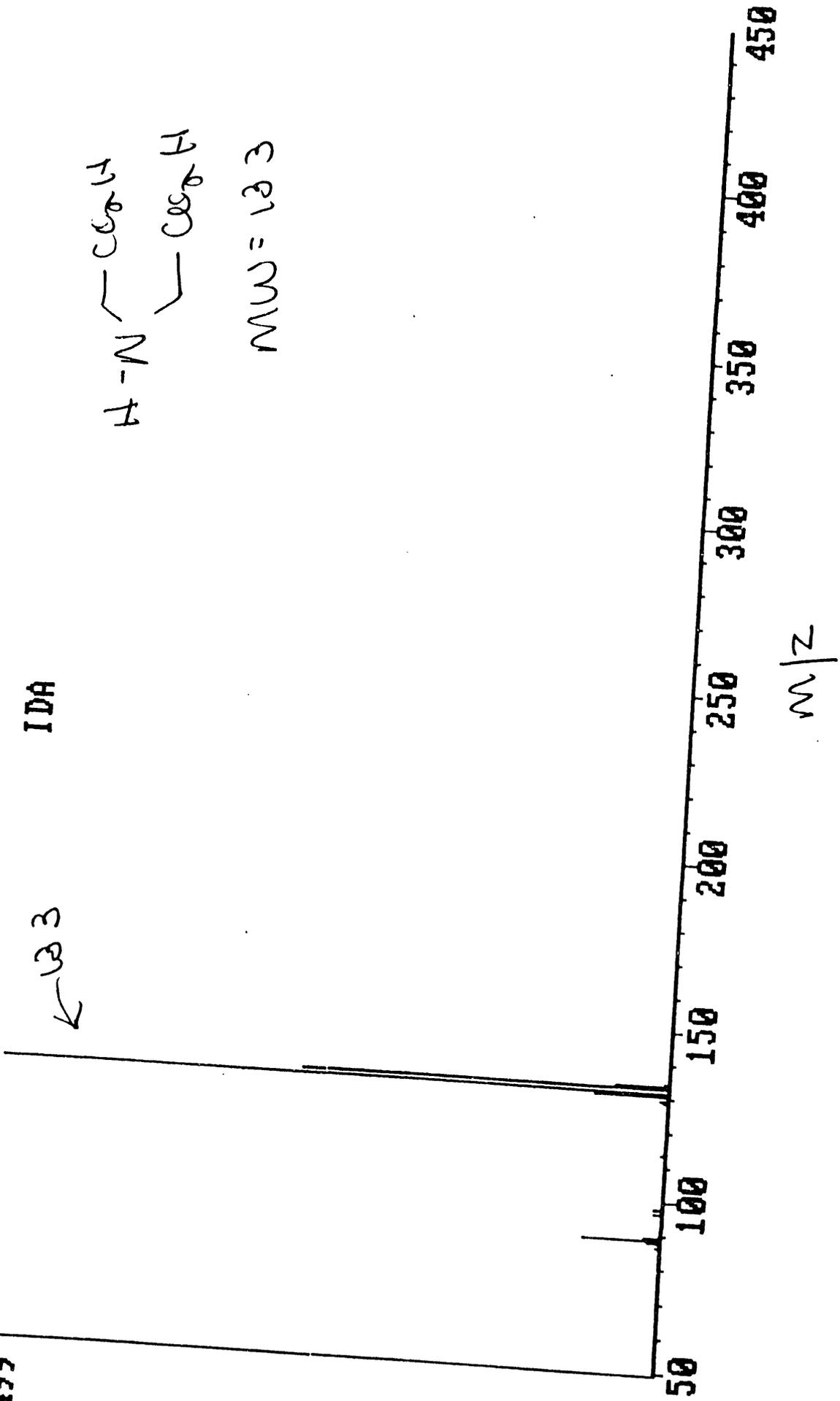
phenanthrene

18499 IDA

← 133



MW = 133



Appendix J

Tank 101-SY Gas Accumulation and Release Physical and Numerical Modeling

**TANK 101-SY GAS ACCUMULATION & RELEASE
PHYSICAL & NUMERICAL MODELING**

T. M. Burke

WESTINGHOUSE HANFORD COMPANY

November 11, 1991

Presentation to the Tank Waste Science Panel

OUTLINE

- Overview of modeling activities
- Simulation of tank rollover
 - Physical model (dynamic simulants)
 - Numerical model
- Modeling of Tank 101-SY Mitigation
 - Physical
 - Numerical

OBJECTIVES OF TANK MODELING

- **Develop improved understanding of rollover phenomenon including gas trapping and release mechanisms**
- **Evaluate/demonstrate/develop potential mitigation concepts**

TANK 101-SY MODELING - "DIVISION OF LABOR"

■ Westinghouse Hanford Company

- Physical modeling with dynamic simulants (rollover and mitigation)
- FATHOMS/GOTHIC numerical modeling (rollover and mitigation)
- Overall responsibility for mitigation development

■ Pacific Northwest Laboratory

- Physical modeling with chemical simulants (rollover and mitigation - emphasis on details of gas trapping & release mechanisms)
- TEMPEST numerical model development
- Assist WHC in developing mitigation concepts

SIMULATION OF TANK ROLLOVER

REASONS FOR DYNAMIC SIMULANT TESTING

- **Allows good control of physical properties (e.g., Particle size and fluid viscosity)**
- Allows reproduction of tank waste physical properties**
- Allows definition of conditions which lead to or prevent gas accumulation/rollover**
- **Simplifies laboratory procedures (test preparation & cleanup; equipment/material compatibility)**
- **Probably leads to reduced time and cost**
- **Large scale testing of mitigation by mixing concepts may be required**
- Not likely to be done with chemical simulant, therefore dynamic simulant must be developed**

DYNAMIC ROLLOVER SIMULATION - MATERIALS/METHODS

Particulates Utilized:

corn meal (initial demonstration)
lime
fly ash
bentonite clay

Gas Generation Methods:

yeast/sugar (initial demonstration)
carbon dioxide saturation/vacuum release
thermal decomposition of baking soda (N_aHCO_3)

DYNAMIC ROLLOVER SIMULATION - RESULTS TO DATE

- General phenomenon of gas trapping/tank rollover/gas release has been demonstrated in a variety of materials
- Details of phenomenon depend on materials used
- Stable thermal inversion phenomenon has been reproduced

DYNAMIC ROLLOVER SIMULATION - FUTURE WORK

- Continue to develop improved simulation
 - Tank core sample data
 - Data from chemical simulants
 - Data from gas release events
- Utilize physical model test results to validate numerical model of rollover phenomenon

NUMERICAL MODELING OF TANK ROLLOVER

- **Modified FATHOMS/GOTHIC Code utilized**
 - Derived from COBRA-NC
 - Three fields included (liquid, gas, particles)
 - Non-Newtonian fluid behavior incorporated (includes mixture viscosity as a function of particle concentration)
- **Two dimensional simulation**
- **Current analysis utilizes best available information for Tank 101-SY (1986 bottle samples)**
- **Sensitivity to input parameters evaluated**

PROPERTIES UTILIZED IN FATHOMS/GOTHIC ANALYSIS

<u>PARAMETER</u>	<u>VALUE</u>	<u>COMMENTS</u>
Particle Size	0.001 inch (25.4 μ m)	Arrived at by numerical Experimentation. New data indicate Sauter Mean of 0.00067 in (16.97 μ m)
Particle Dens.	133.3 lbm/ft ³ (2135 kg/m ³)	Derived from specific gravities.
Convective Layer Specific Grav.	133	1989 Measurements
Non-convective layer sp. gr.	1.69	1989 Measurements
Maximum Mixture Viscosity	10,000 lbm/ft-s (1.48e6 poise)	Arrived at by numerical experimentation. No new data. However, shear strength gives an effective viscosity of this size for: the calculated strain rates.
Shear Strength	1209 lbm/ft-s ² 18,000 dyne/cm ²	New measurements show shear strength around 5,000 to 10,000 dyne/cm ²

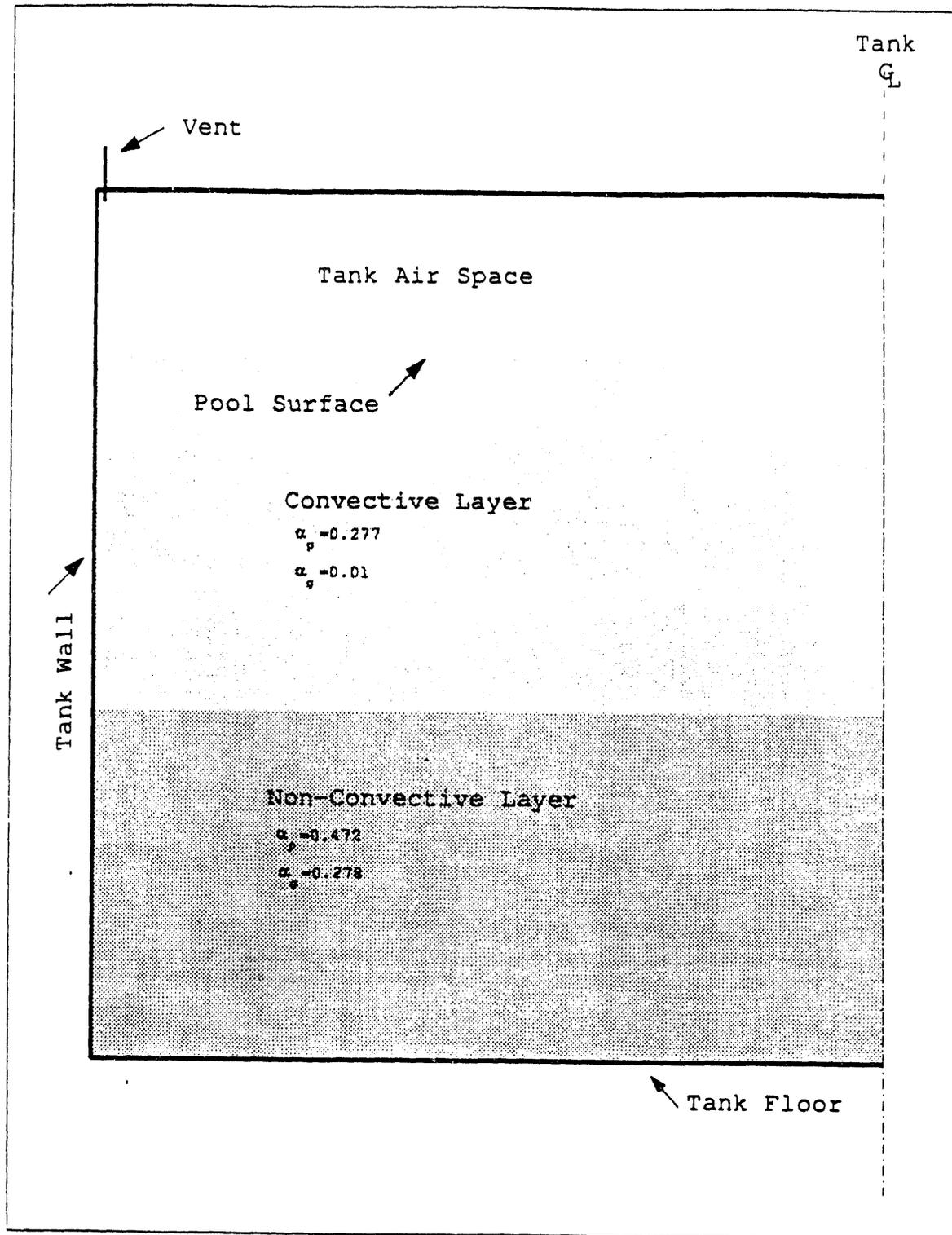


Figure 4.3 Two-dimensional Slab Model - Initial Conditions.

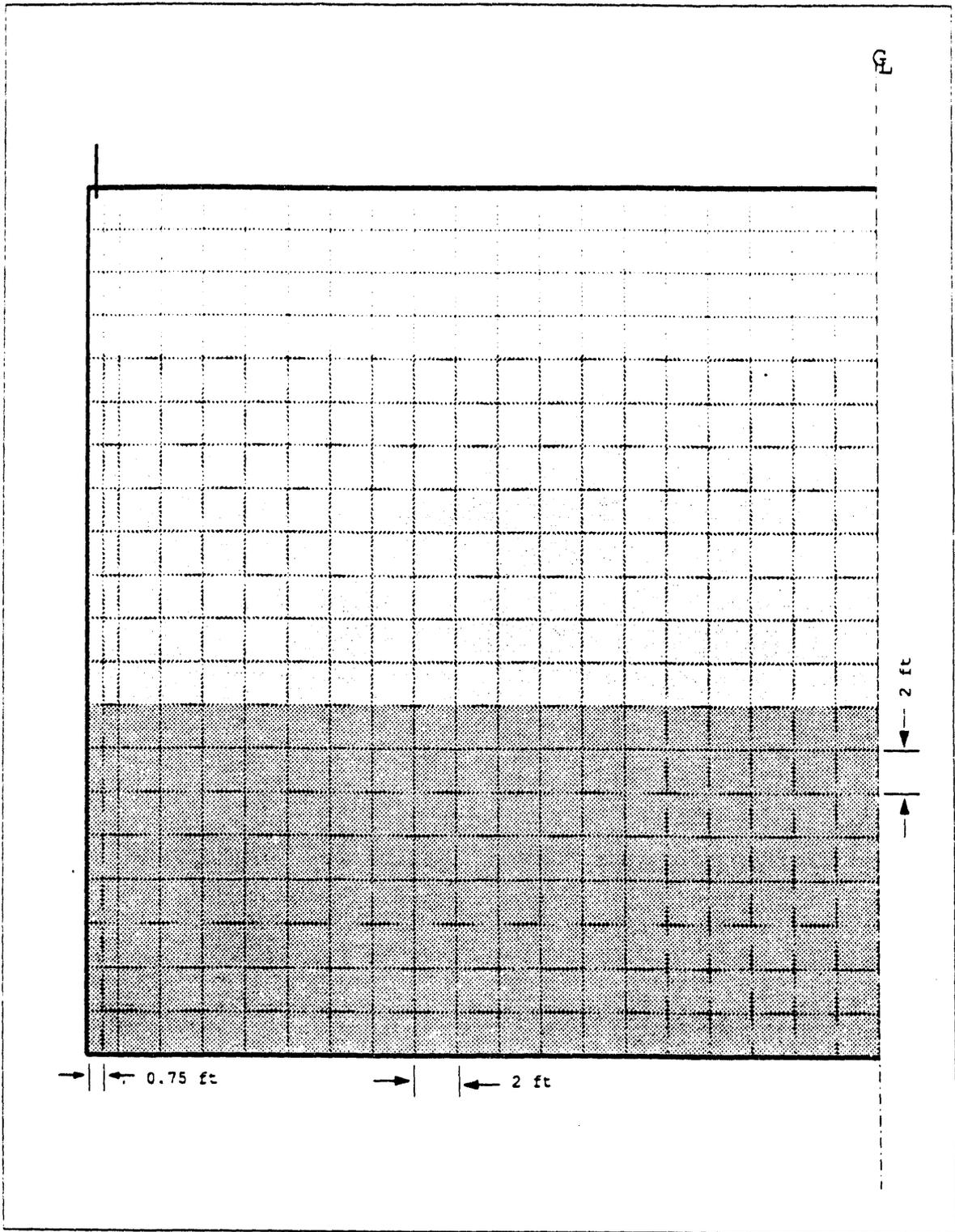
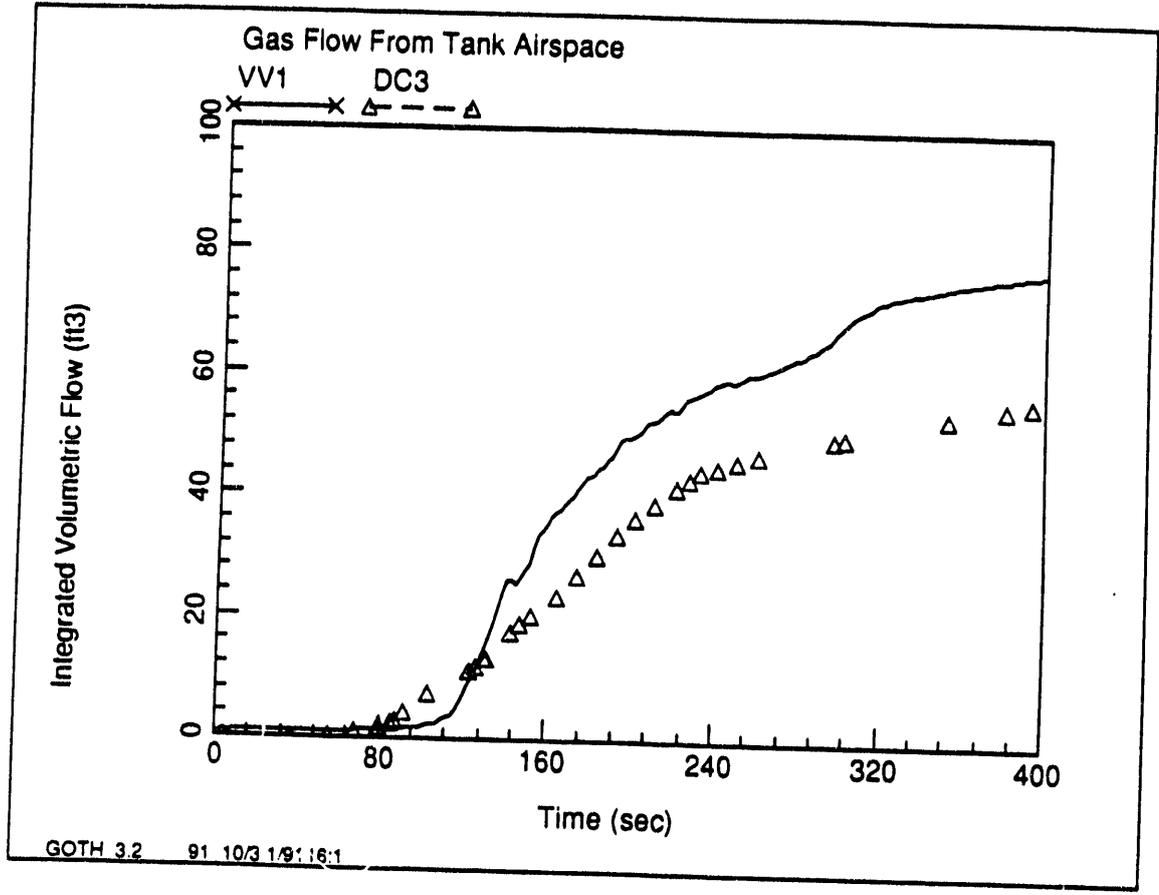
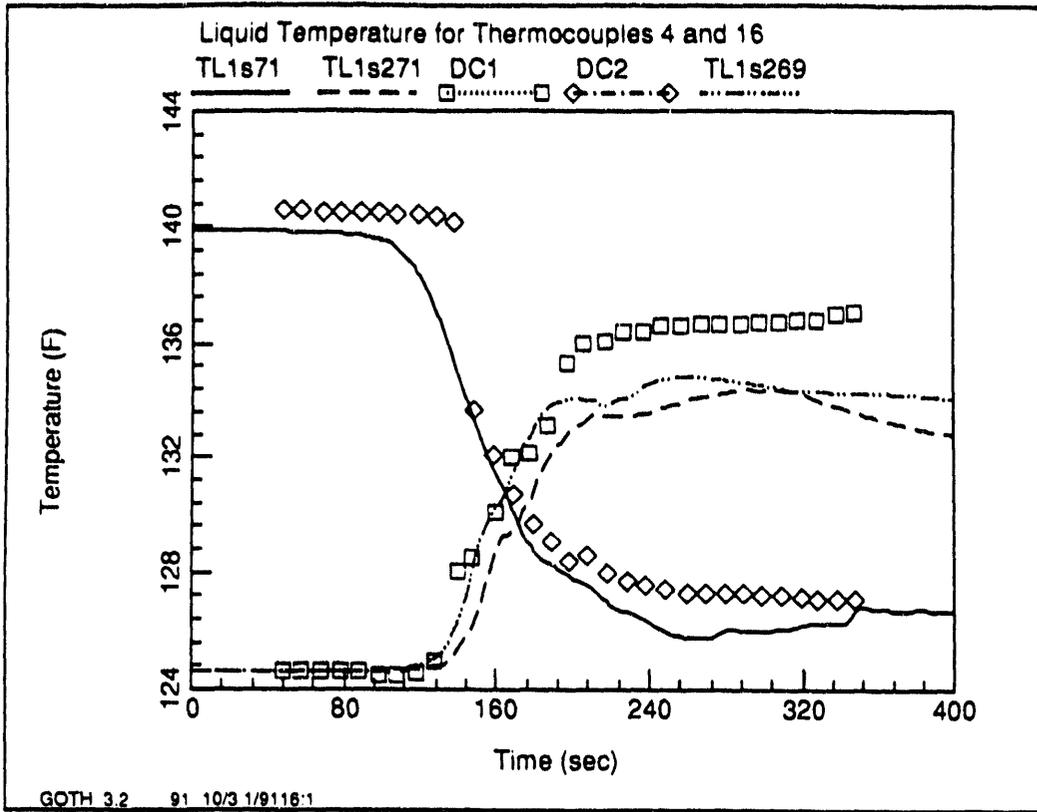


Figure 4.4 Computational Mesh for Two-dimensional Slab Model.





CONCLUSIONS FROM NUMERICAL MODELING

- Overall results from the numerical model agree well with observations
 - Gas release quantities
 - Temperature inversion
- Results of the calculations are sensitive to material properties utilized
 - Small particle size required
 - High mixture viscosity and/or shear strength required
- Recent data from core samples appear to confirm material properties suggested by numerical model
- A significant volume of gas may be retained in slurry after rollover

NUMERICAL MODELING OF ROLLOVER - FUTURE WORK

- Update simulation to utilize three dimensional model and data from Window C core samples
- Validate model by comparison to:
 - Data from TANK 101-SY
 - Physical model test results
- Update model as appropriate
- Utilize model in future evaluations
 - Safety assessments/SAR updates
 - Evaluation of mitigation concepts

MODELING OF TANK 101-SY MITIGATION

MITIGATION OF PERIODIC GAS RELEASE

- Continuous or high frequency release will result in hydrogen concentration well below lower flammability limit
- Several potential concepts under evaluation:
 - Ultrasonic agitation (external or internal)
 - Chemical treatment
 - Surfactant addition
 - Dilution
 - Heating
 - Tank mixing
 - Mechanical stirrers
 - Inert gas sparging
 - Pumps
 - Other fluidic devices

OBJECTIVES OF INITIAL MITIGATION BY MIXING TESTING

- **Develop basic understanding of transient mixing/suspension process**
- **Evaluate relative effectiveness of potential mixing concepts**
 - e.g., continuous versus periodic jet**
- **Provide data for numerical model validation**
- **Develop recommendations for next stage of development and testing**

DESCRIPTION OF CURRENT MIXING TESTS

- 1/10 Scale, 30° sector lucite test section utilized
 - Relatively large scale but small volume
 - Allows good visual observation
 - Results apply directly only to configurations with 30° symmetry
 - Possible side wall effects
- Same particulates developed for rollover tests being utilized. Tracer particles added to improve visualization
- Methods of quantifying slurry mobilization being developed
- Testing just now beginning

NUMERICAL MODELING OF MITIGATION BY MIXING

- Modeling to date performed by PNL with TEMPEST code
- WHC developing capability to utilize TEMPEST
- Some analyses likely to be performed with FATHOMS/GOTHIC:
 - More sophisticated treatment of particulates
 - Less sophisticated turbulence model
 - Importance of results demands verification

SUMMARY

- Considerable progress has been made in understanding and modeling the Tank 101-SY rollover phenomenon
- Additional work is required to improve and confirm the existing models
- Emphasis is shifting to evaluation of mitigation concepts
- Mitigation concept development requires:
 - Tank samples
 - Physical modeling (dynamic & chemical simulants)
 - Numerical modeling

Appendix K

Ultrasound Slurry Degassing for Mitigation of 101-SY

**Ultrasound Slurry Degassing
for Mitigation of 101-SY**

Science Panel Meeting

*11-12 November 1991
Richland, WA*

presented by

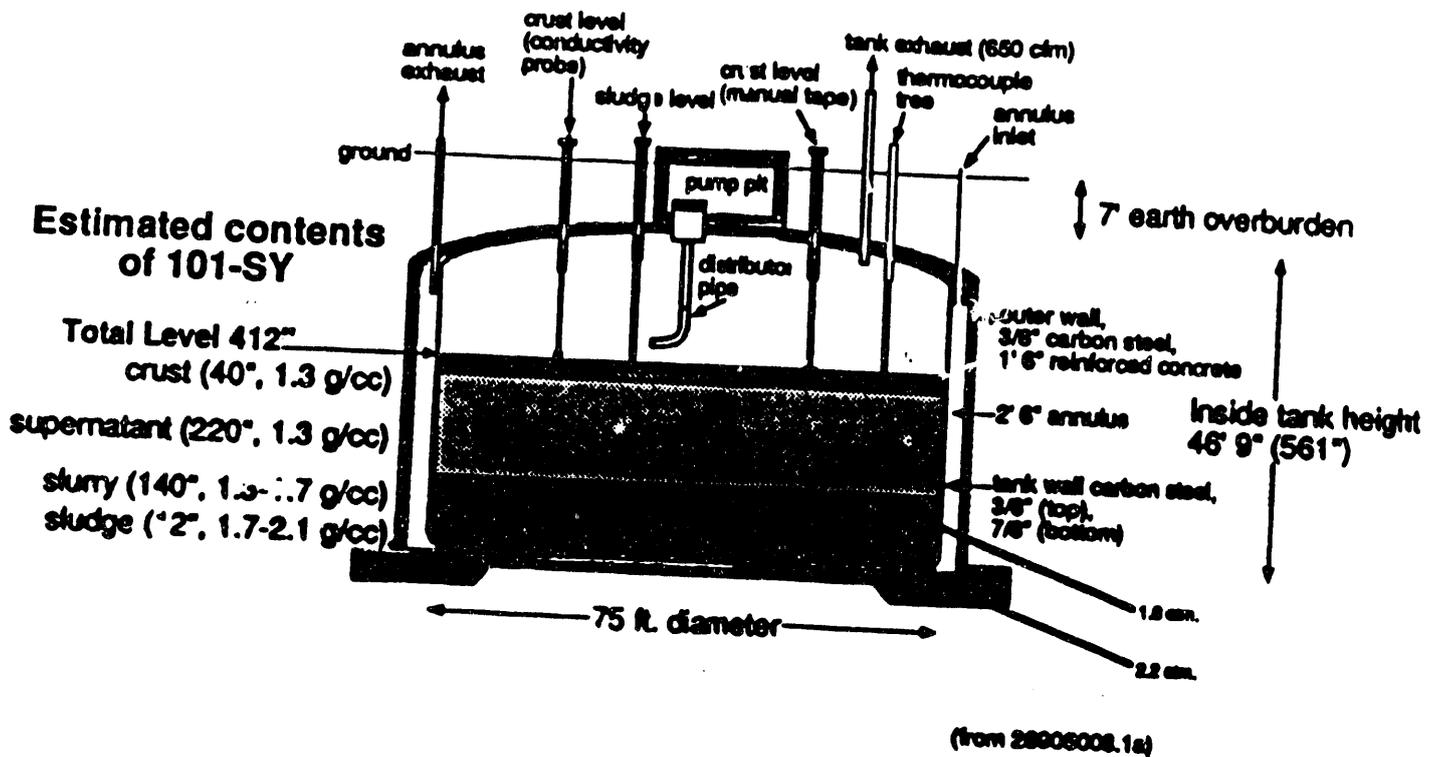
Stephen F. Agnew
Mail Stop C346, Group INC-4
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Los Alamos, NM 87545

phone: (505) 665-1764
fax: (505) 665-3166

11/10/91 Predecisional Draft—Review Purposes Only

OS Alamos

Typical Double Shell Tank



Composition of Layers

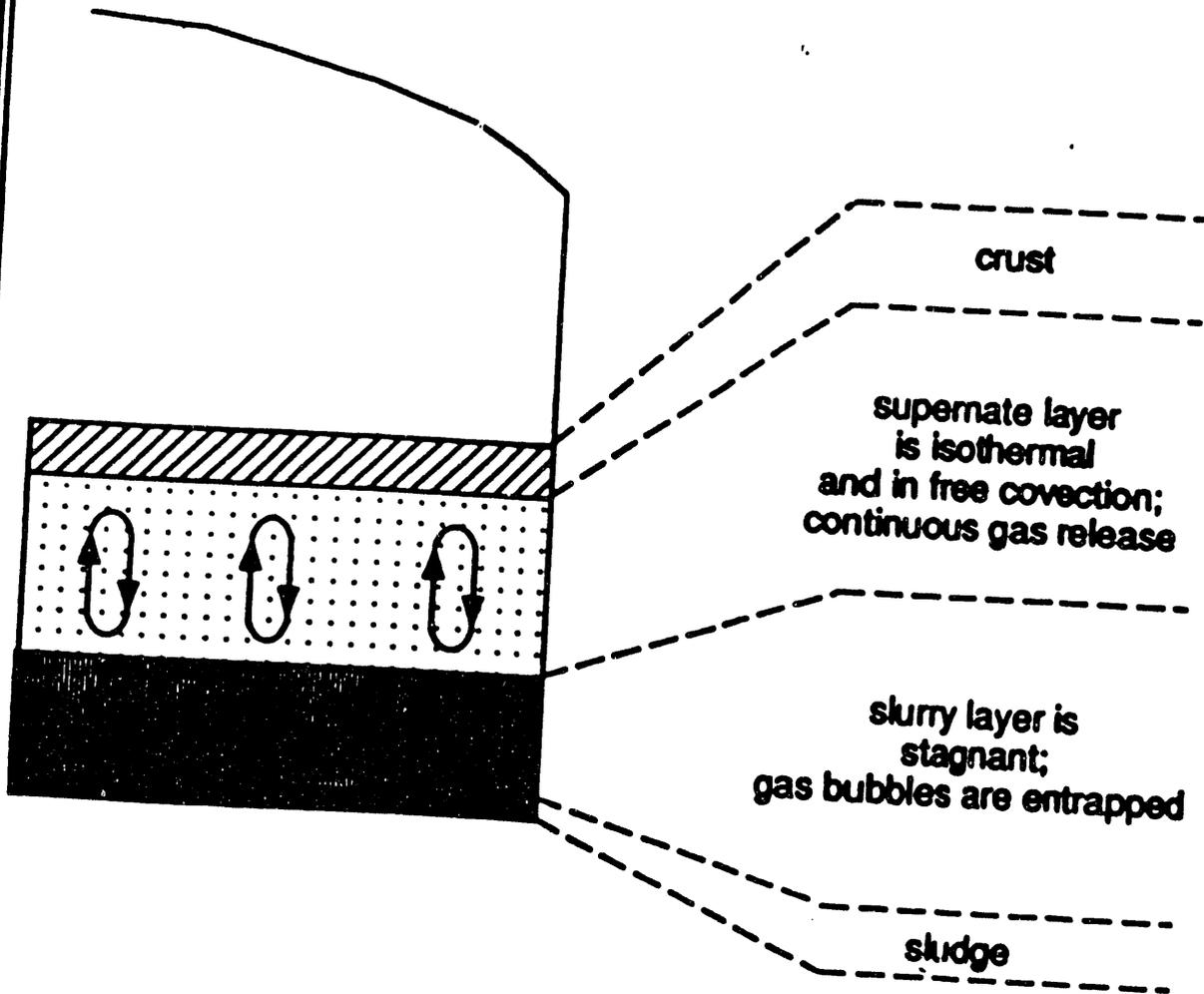
Crust—low density solid form of slurry particles, 1.3 g/cc (floats on supernate).

Supernatant—saturated aqueous nitrate, nitrite, carbonate, aluminate, as well as organics, 60-80% water, 1.3 g/cc.

Slurry—suspended particles comprising sodium aluminate/nitrate/nitrite/carbonate, ~10 μm particle size, 40-60% water, 1.3-1.7 g/cc.

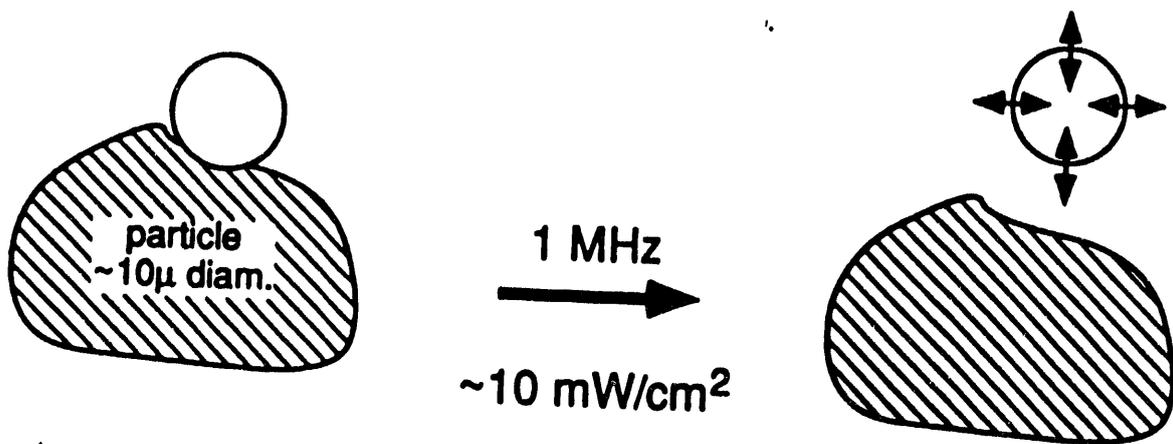
Sludge—larger particles (>10 μm particle size), sodium aluminate/nitrate/nitrite/carbonate, metal hydroxides/carbonates (Fe, Ca, Ni, Cr), 20-40% water, 1.7-2.2 g/cc.

**Gas Bubbles are entrapped in
non-convecting slurry layer**



os A amos

Actively Excite Monopole Modes of Bubbles

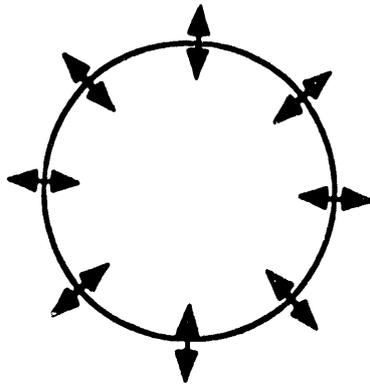


Bubbles are "mobilized",
effectively "pinned" to that
size, and will not nucleate.

Los Alamos

Monopole Bubble Frequency

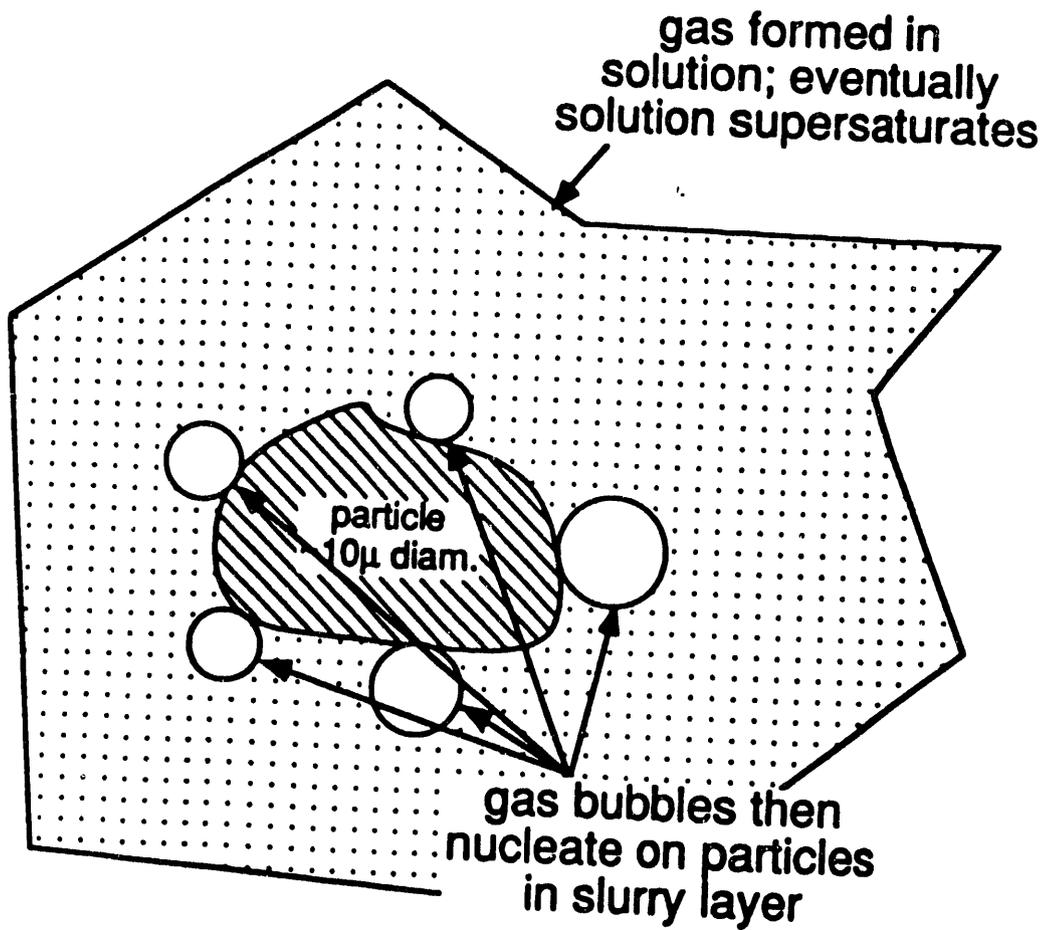
totally symmetric mode of bubble



1 μ bubble in water at 1 atm.
is \sim 1 MHz

os Aramos

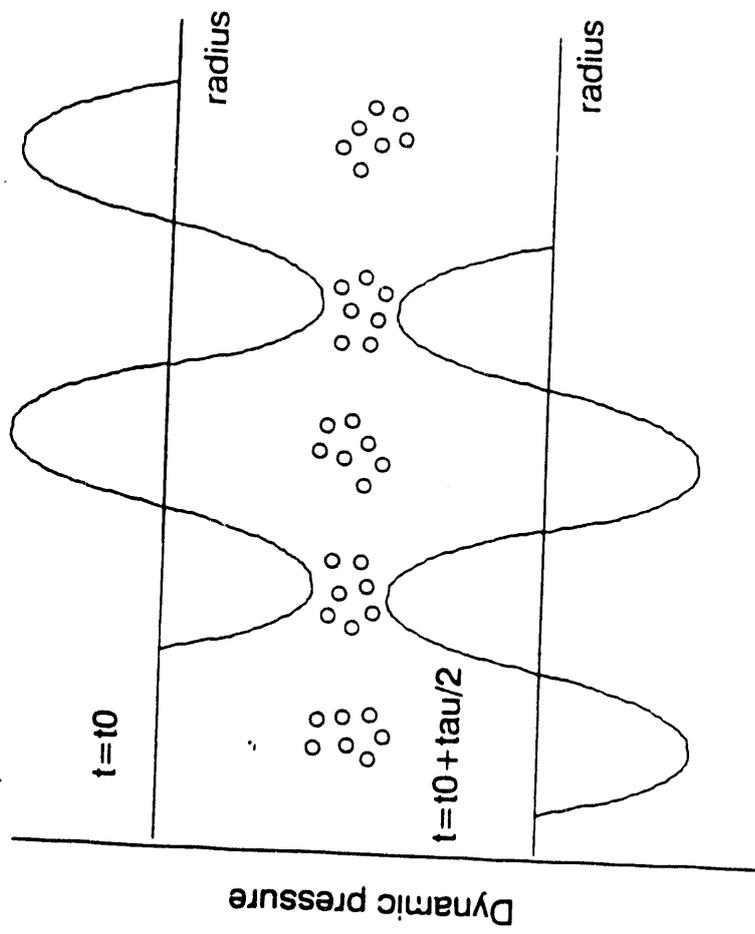
Bubble Formation in 101-SY



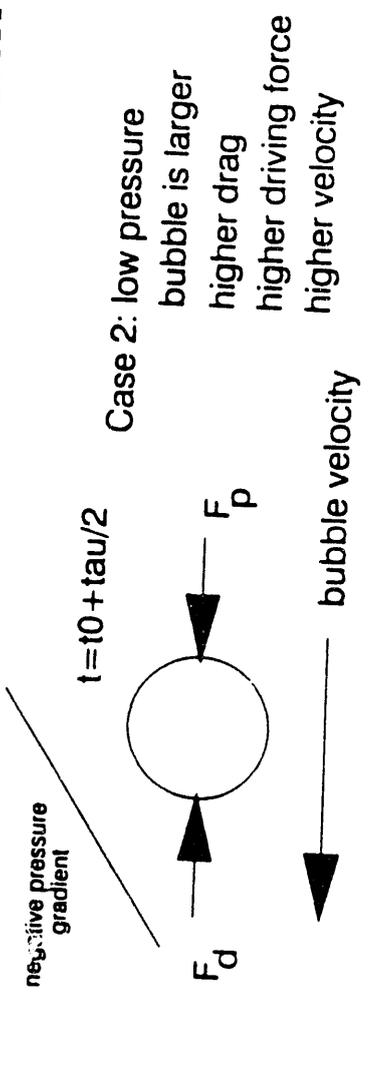
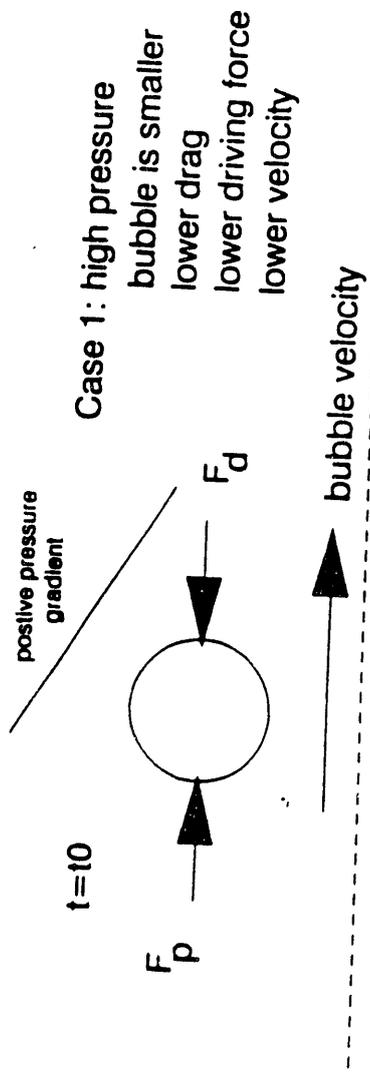
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MEE-13 ENGINEERING MECHANICS LOS ALAMOS



MEE-13 ENGINEERING MECHANICS LOS ALAMOS

Description of Project

Overall goal:

Use ultrasound and/or acoustic active transducers to control bubble nucleation and prevent gas entrapment in the non-convecting slurry layer of 101-SY.

Three primary tasks:

- Design, build, and instrument model tank.
- Reproduce slurry swelling in simulated waste tank.
- Perform passive and active ultrasound and acoustic measurements on simulated waste in model tank.
- Adapt existing computer programs to model low frequency acoustic behavior of model tank as well as 101-SY.

Need to integrate with WHC and PNL on their acoustic monitoring scheme.

Three primary tasks:

- Design, build and instrument model tank.
 - 18" in diameter
 - approximately 34 L total volume
 - pressurizable to simulate liquid column of 101-SY
 - internal heater to simulate radiolytic heat generation
 - continuously monitor temperature and crust height
 - must simulate slurry growth and bubble entrapment

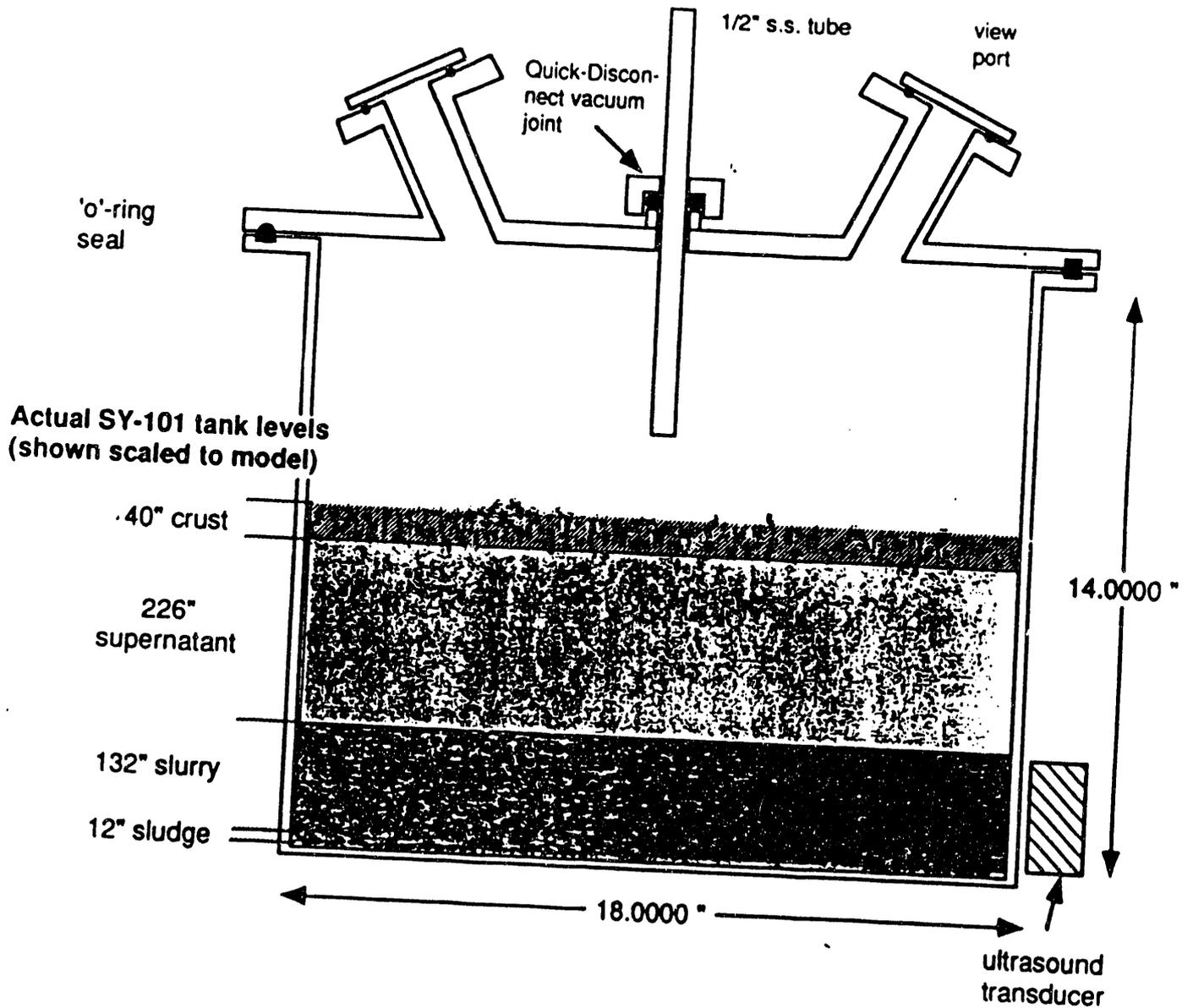
- Perform passive and active ultrasound and acoustic measurements on simulated waste in model tank.
 - determine effectiveness of ultrasound to control bubble nucleation
 - optimize frequency, power, and pulse character for that control
 - investigate use of low frequency modes to sweep bubbles out of tank

- Adapt existing computer programs to model low frequency acoustic behavior of model tank as well as 101-SY.
 - measure acoustic properties of model tank
 - measure acoustic properties of large tanks similar in size to 101-SY
 - construct computer models of tanks using ABACUS code
 - determine transducer placement for active excitation
 - determine effectiveness of sweeping bubbles using acoustic drivers

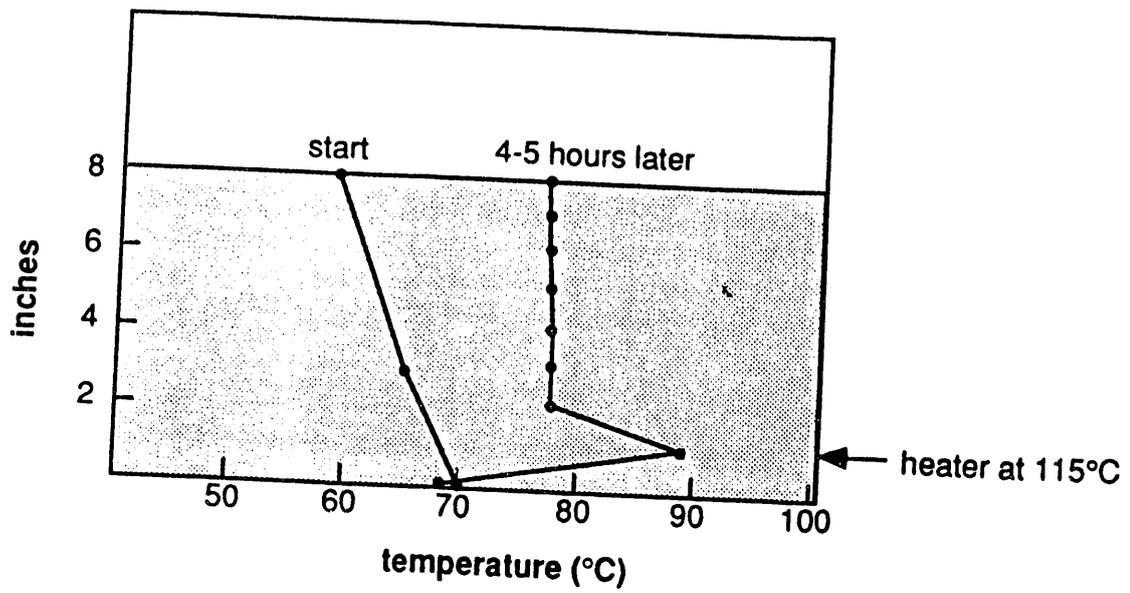
Model HLW Tank

Use stainless steel, 18" dia. 3/8" wall,
w/ bottom 3/8" welded plate,
rim 1/2" disk, top 3/8" plate.

Leak check tank to vacuum and 70 psi.



thermal profile in model waste tank



Status

Tank is completed

Instrumentation in place.

- heater at 1.8" depth, 500 watts.
- TC readout as function of depth, per inch.
- fast time response pressure transducer (0.5 sec).
- acoustic level monitor (± 1 mm).

Instrumentation now being installed.

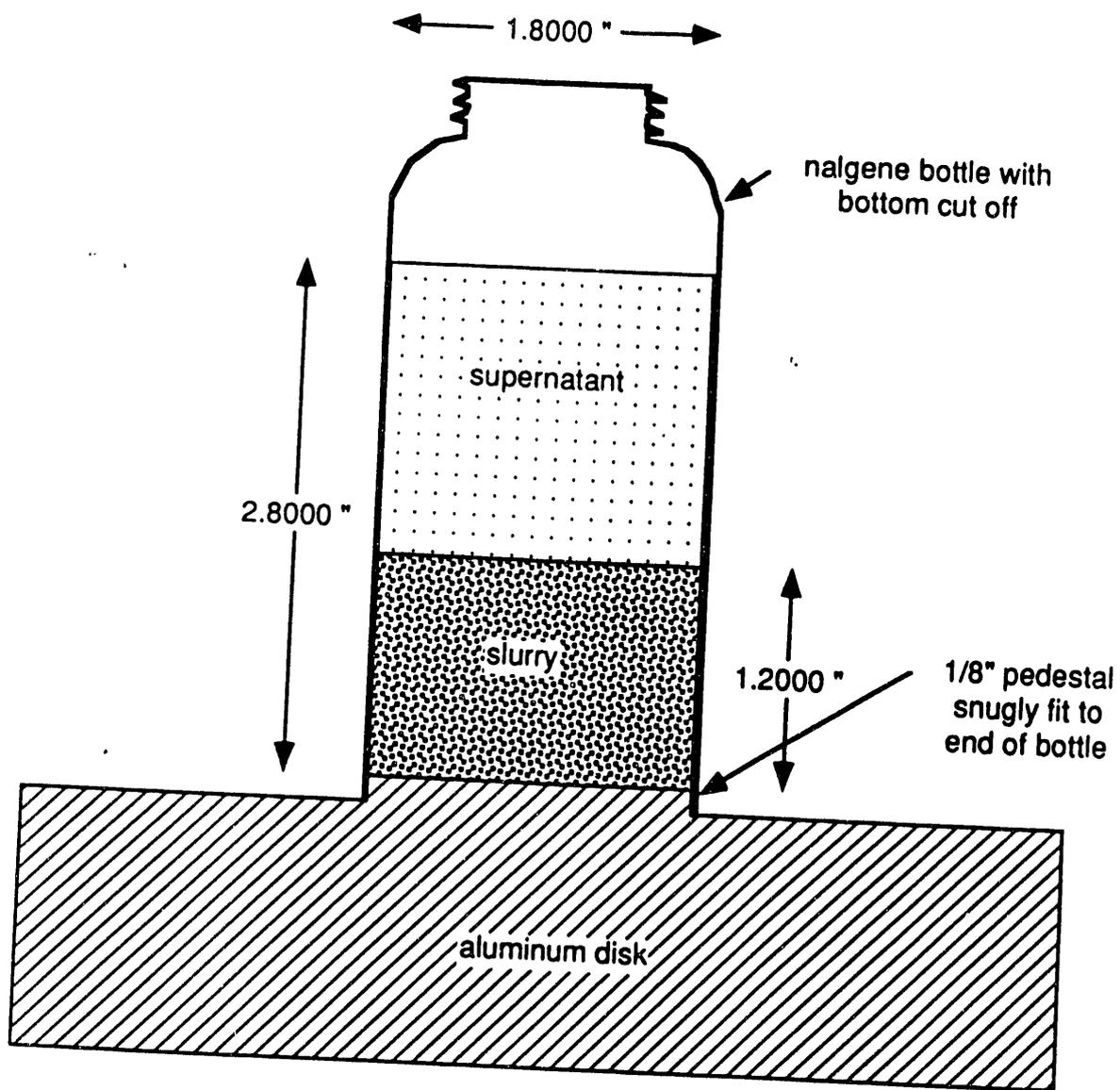
- all data to computer station.
- waveguide for 50 kHz ultrasound.

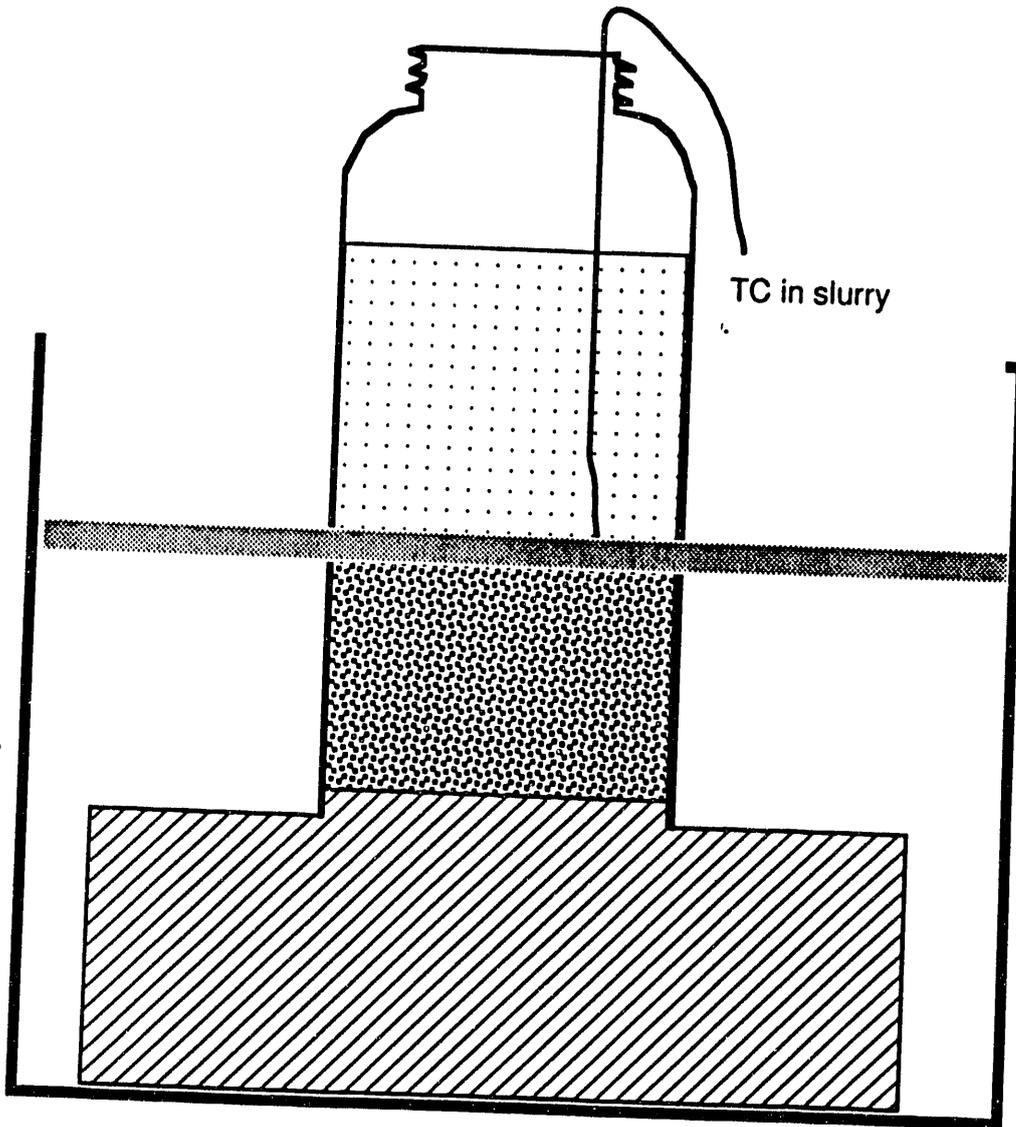
Tank constituents are:

- NaNO₃ 3.73 M
- NaNO₂ 3.55 M
- NaOH 3.49 M
- NaAlO₂ 2.27 M
- Na₂CO₃ 0.53 M

- Na₄EDTA 0.12 M (50 g/L)
- Na₃HEDTA 0.13 M (50 g/L)

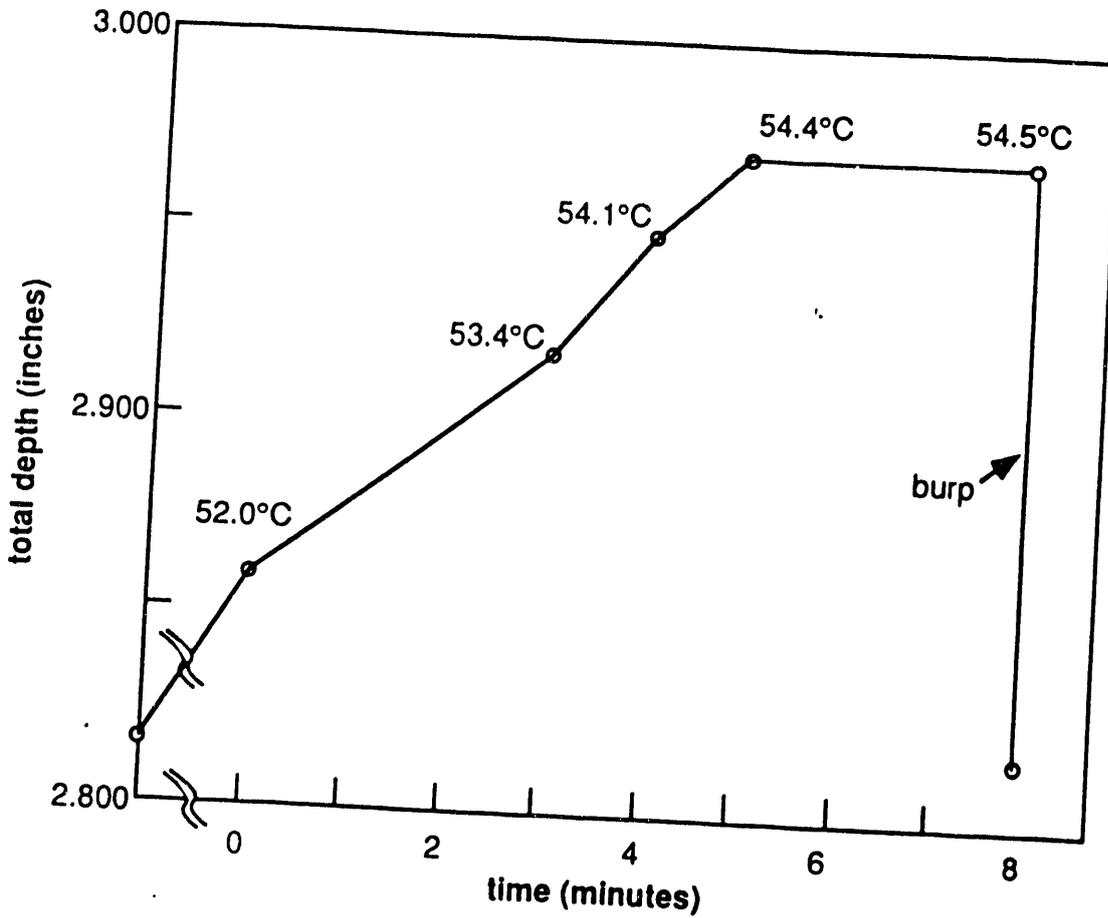
Model for slurry swell





thermostatted ultrasonic water bath

Level in 1.8" diameter bottle, aluminum bottom
slurry depth 1.2" at start



total rise $0.150"/1.2" = 12.5\%$ of slurry
(rise in 101-SY $10"/140" = 7\%$ of slurry)

Initial results

—use reaction of caustic with aluminum plate for homogeneous gas production.

—demonstrated proof of principle; ultrasound degases simulated slurry.

—depressurization leads to slurry compaction.

—temperature of slurry is critical in process of entrapment.

—large viscosity change around 50-60°C due to precipitation of NaNO_2 salt.

—gas evolution only at higher temperatures, 100-110°C.

—sound speed 1,900 m/sec at 60°C.

—attenuation about 30% over three feet at 2.5 MHz (from side of tank).

—ultrasound trapped in bottom 1" layer when excited from bottom of tank

—crust density ~1 g/cc

Further results...

—slurry swelling occurs only when very small bubbles are generated.

—estimate of average bubble size is $50\ \mu$, with a range from $30\text{-}150\ \mu$ (from direct observation of slurries swollen by gas from aluminum reaction).

—monopole resonance of $50\ \mu$ bubble is $47\ \text{kHz}$ (pressure $595\ \text{torr}$, solution density of $1.5\ \text{g/cc}$).

—in 101-SY at $2.4\ \text{atm}$, $82\ \text{kHz}$ for $50\ \mu$ bubbles.

—wavelength of $50\ \text{kHz}$ is $3.8\ \text{cm}$.

—repeated tries at volumetric gas production have failed.

—aluminum plate in $18''$ tank is too vigorous; will need to scale it back.

Future work...

- Get the slurry swelling to work in 18" tank, reproducibly and consistently.
- Use computer to record temperature profile, pressure, and level as function of time.
- Demonstrate effectiveness of ultrasound at 50 kHz.

Secondary effects that could result in problems...

1) heating

—must keep total sonic energy less than than the ~10% of 12 kW radiolytic load.

2) particle streaming, alignment, or fracture

—could corrode waveguide

3) sonochemistry

—chemistry is attributed to radicals that are created by cavitation.

—since *same* radical chemistry is also induced by radiolysis, as long as excitation power levels are fraction of radiolytic load.

—in fact, we will be far below cavitation levels, except near the waveguides.

—cavitation near the waveguides will likely lead to some electrode erosion.

Secondary effects that could help...

1) heating

—evidence indicates holding power of slurry is strongly temperature dependent.

2) particle streaming, alignment, or fracture

—homogenization of supernatant and slurry.

—particle alignment will weaken slurry.

3) sonochemistry

—getting rid of organic will also solve problem.

Sonochemical Issues

- gas production

—are gases same or not? This we can answer.

- other chemical species

—this will be more difficult, but I believe unnecessary, since radiolysis should yield same products.

Review of Russian work...

M. A. Margulis, Zh. Fiz. Khim., 48, 2968-73 (1974)

—formation of nitrite from nitrate with 4.5 w/cm² at 1 MHz (acoustic power from decomposition of chloroacetic acid).

—cavitation induces radical chemistry very similar to radiolysis (hydroxyl radicals and solvated electrons).

—no more nitrite after one hour under hydrogen.

—maximum nitrite 1.6e-5 M with nitrate 1e-2 M.

—peroxide production rate depressed with high pH, from 1e-5 M/min to 2e-6 M/min at pH = 13.5.

Safety Issues with Use of Aluminum in Simulated Waste

- Limit total amount of aluminum such that reaction heat will only vaporize 5% of water.
- Assuming $3/2$ mol gas for each mol Al, limit total amount of gases produced.
- Limit total area of aluminum to 0.14 area of base for 18" tank (size dependent).

Results in 18" diameter tank with aluminum plate...

—got consistent swelling of about 1/4" over pressure range 300-1200 torr (0.4-1.6 atm.).

—turnovers occurred at lower pressure, but were still sporadic—need time to set slurry.

—after three hours, aluminum plate reacted vigorously in 18" diameter tank.

—future experiments with aluminum wire, limiting surface area as well as total aluminum to prevent too vigorous of a reaction.

Appendix L

Physical Modeling of Tank 101-SY Phenomena with Chemical Stimulants

TANK WASTE SCIENCE PANEL MEETING NOVEMBER 11-13, 1991

**PHYSICAL MODELING of TANK
101-SY PHENOMENA with
CHEMICAL SIMULANTS**

**R.T. ALLEMANN
ANALYTIC SCIENCES DEPARTMENT**

**Pacific Northwest
Laboratory**

- **GOAL - Observe gas retention and release to ascertain the more fundamental physical mechanisms and improve the modeling and analysis of mitigation.**
- **APPROACH - Introduce gases into synthetic waste which is similar in composition and form to 101-SY slurry.**

CURRENT SCOPE

BENCH SCALE TESTING

Method

**4 inch diameter plastic tanks.
Increase scale when appropriate.**

GAS GENERATION

- **Intrinsic**
- **Hydrogen from aluminum - caustic reaction**
Aluminum vessel floor
Dispersed aluminum chips
- **Sparger**

SYNTHETIC WASTE PROPERTIES

- **The mixed chemicals form a slurry that slowly produces gas.**
- **The slurry must be "thermally conditioned" to form a supernatant and sludge.**

SYNTHETIC WASTE PROPERTIES cont.

- **Conditioning is a (heating and cooling) process in which crystals are formed and then sink to give a sludge layer on the bottom.**
- **During conditioning some intrinsic gas rises to a floating layer akin to the 101-SY tank crust.**

SYNTHETIC WASTE PROPERTIES cont.

- **When cooled, the sludge layer is cohesive**
- **When cooled, visible crystals form in the supernant**

RESULTS

Testing the hypothesis of sludge strength sufficient to retain interspersed gas

- **Sludge does trap gas.**
- **Yield strength of in situ sludge is high when cool but decreases on heating.**

RESULTS cont.

- **Crystal formation is temperature dependent.**
- **Crystal morphology is consistent with cohesive strength.**

USES OF DATA AND TESTING

- **To have strength/temperature data which can be incorporated in release model and mitigation codes.**
- **To help engineer the mitigation methods of mixing, heating, etc., according to the viable hypothesis of the physical mechanism.**

USES OF DATA AND TESTING cont.

- **To devise new or more refined mitigation methods.**
- **To define property ranges appropriate for physical modeling with dynamic simulants.**

FURTHER WORK

- **Microscope study to determine physical reason for strength/change with temperature.**
- **Quantify physical properties variation with temperature.**
- **Test mitigation techniques.**

CONCLUSIONS

Physical modeling experiments using chemical simulants

- **Obtaining physical properties that are required to promote and support the engineering of a successful mitigation method.**

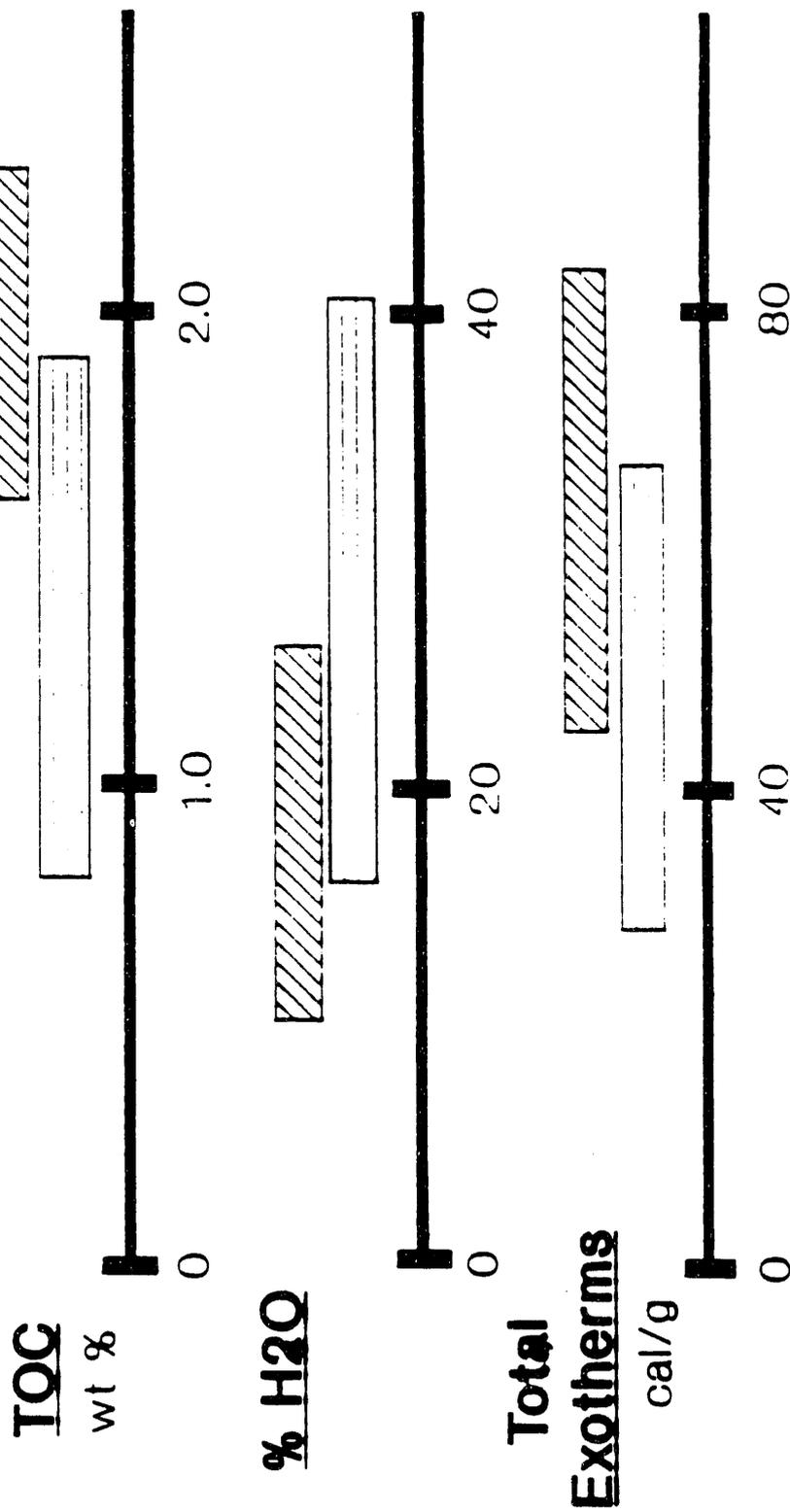
Appendix M

Comparison of Window A and Window C Crust Sample Results

COMPARISON OF WINDOW A AND WINDOW C CRUST SAMPLE RESULTS

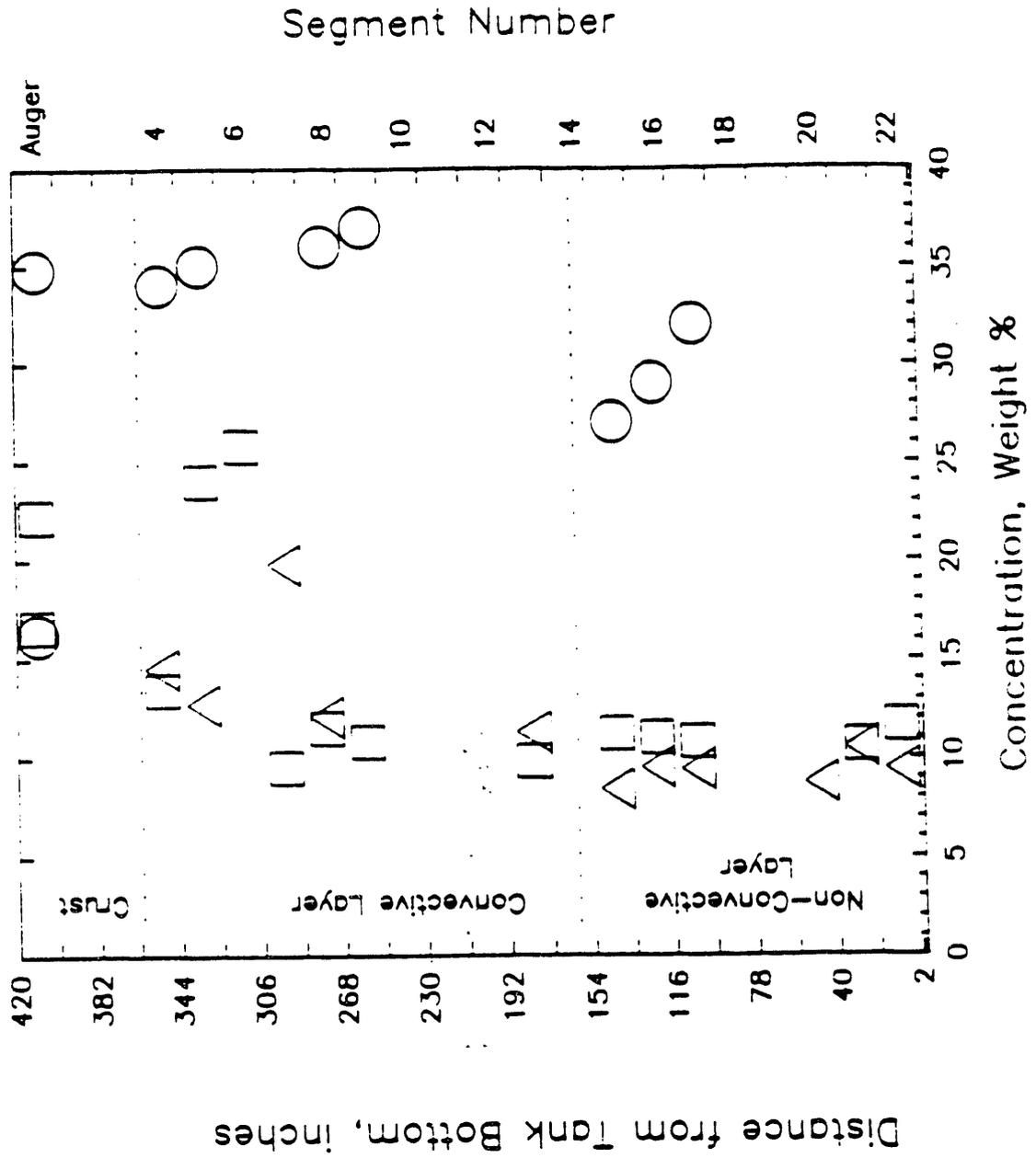
Window A: 

Window C: 

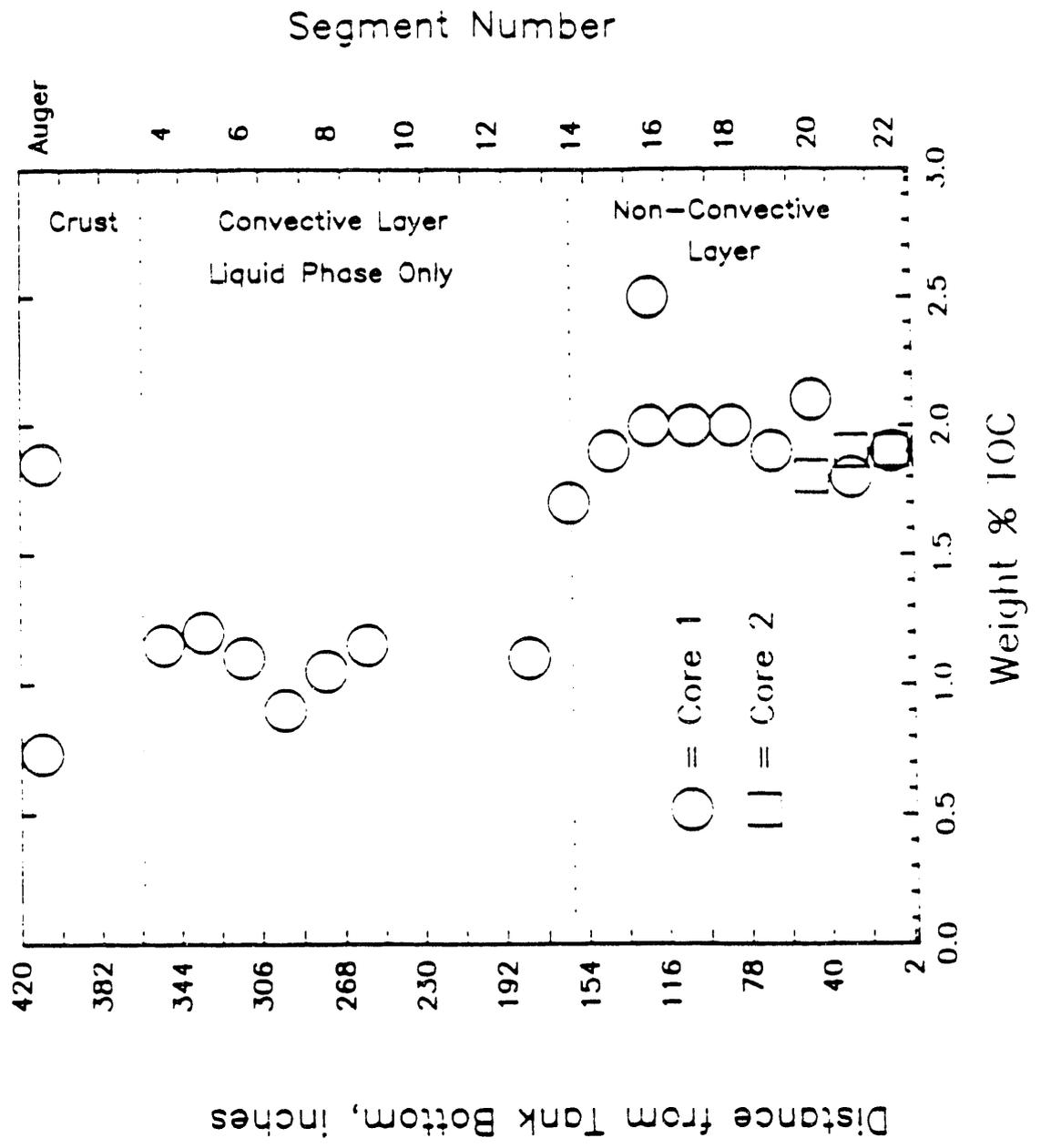


Tank 101-SY Window C

Nitrate, Nitrite, and Moisture



Tank 101-SY Window C Total Organic Carbon



TANK 101-SY CORE SAMPLE

Average Composition by Weight Percent

	Convective Layer	Nonconvective Layer
H ₂ O	35	29
Na ⁺	20	21
Aluminate	12	13
NO ₂ ⁻	12	9
NO ₃ ⁻	10.5	10
TOC	1.2	1.9
Cr	0.006	0.7
Fe	0.002	0.06
Ca	0.005	0.04
Total	91	85
NOT included in total: Organic, H, N, O, OH-, CO ₃ ²⁻ ; C1-, SO ₄ ²⁻ ; K+, etc.		

CRUST BURN ISSUE

- * DATA FOR TOC, MOISTURE, EXOTHERMS SHOW THAT THE POTENTIAL FOR A REACTION IS QUITE LOW**
- * TV CAMERA SHOWS THAT MOST OF THE SURFACE IS LIQUID**
- * WINDOW A PROVIDED SAMPLES FROM THREE TANK "INSTRUMENTS" AND WINDOW C PROVIDED AUGER AND SLUDGE WEIGHT SAMPLES FROM 4 RISERS**
- * ARE ANY OTHER SAMPLES OR DATA NEEDED TO CLOSE THE ISSUE?**

GAS MONITORING STRATEGY

- * FOR THE GAS RELEASE EVENTS:**
 - MEASURE ALL GASES**
 - USE GC, MASS SPEC., GRAB SAMPLES, HYDROGEN MONITORS, CRYOGENIC TRAP, AMMONIA BUBBLER OVM, DRAGER TUBE**

- * BETWEEN EVENTS:**
 - MEASURE ALL GASES**
 - USE GC, GRAB SAMPLES, MASS SPEC.**

- * DOES ANY RATIO OR COMINATION OF GASES GIVE INSIGHT TO PARTICULAR MECHANISMS ?**

MITIGATION/REMEDIATION

MITIGATION: ACTIONS, POSSIBLY REPETITIVE IN NATURE, THAT WOULD BE TAKEN TO REDUCE THE INTENSITY OR SEVERITY OF THE HAZARD.

MITIGATION CONCEPTS:

- **ULTRASONIC AGITATION**
- **DILUTION, MIXING, HEATING**

M.7

REMEDIATION: ACTIONS THAT WOULD BE TAKEN ON THE WASTE FORM THAT ELIMINATE THE SAFETY HAZARD

REMEDIATION CONCEPT:

- **"SEPARATION"**
- **REMOVE CESIUM**
- **SOLVENT EXTRACTION OF SELECTED SPECIES**

MITIGATION

*** OTHER THAN PHYSICAL PROPERTIES, MAJOR ANIONS AND MAJOR CATIONS, WHAT DATA ARE NEEDED FROM THE CORE SAMPLES ?**

*** FOR EXAMPLE, WHY DO ORGANIC ANALYSES?**

SCIENCE PANEL ACTIONS

* NEED PANEL'S POSITION ON MECHANISMS FOR GAS GENERATION, RETENTION AND RELEASE.

- PROVIDE BEST GUESS AT THE END OF EACH PANEL MEETING AND UPDATE AS DATA BECOME AVAILABLE

* NEED RECOMMENDATIONS/COMMENTS ON THE PROGRESS OF WORK. INDICATE WHAT PORTIONS MAY BE OF LOW VALUE AND INDICATE WHAT IS MISSING.

* INPUT FROM PANEL IS VALUABLE, BUT IT MUST BE TIMELY.

* DRAFT MINUTES NEEDED IN 3 WEEKS AND FINAL REPORT SHOULD BE COMPLETED IN SIX WEEKS FOR EACH MEETING.

Appendix N

Ferrocyanide Stabilization Program Working Group Coordination Meeting

**Hanford Site
Ferrocyanide Stabilization Program
Working Group Coordination Meeting**

Waste Tank Science Panel Meeting

**R. J. (Bob) Cash
Westinghouse Hanford Company
November 12, 1991**

CURRENT DIRECTION OF FERROCYANIDE PROGRAM

Current Understanding:

- In situ safe storage of ferrocyanide in tanks will be safe
- Compositions of waste in tanks are probably not reactive

Key Factors (Criteria): What is the safety envelope?

- Temperature of tank waste
- Moisture content of waste
- Concentration of ferrocyanide in the waste

FERROCYANIDE PROGRAM (Continued)

Surveillance and Controls:

- **Temperature monitoring and OSR limits will be required**
 - **Thermocouple trees only sense temperatures up to 10' away**
 - **Infrared scanning probably not feasible due to surface roughness**
 - **Do we rely on hot spot modeling and forget temperature monitoring?**
 - **What are the alternatives, politics, bureaucracy, etc.?**
- **In situ moisture monitoring and OSR limits will be required**
 - **Need NDT moisture monitoring technique**
 - In-tank probe or Liquid Observation Wells**
 - **Is the waste hygroscopic?**

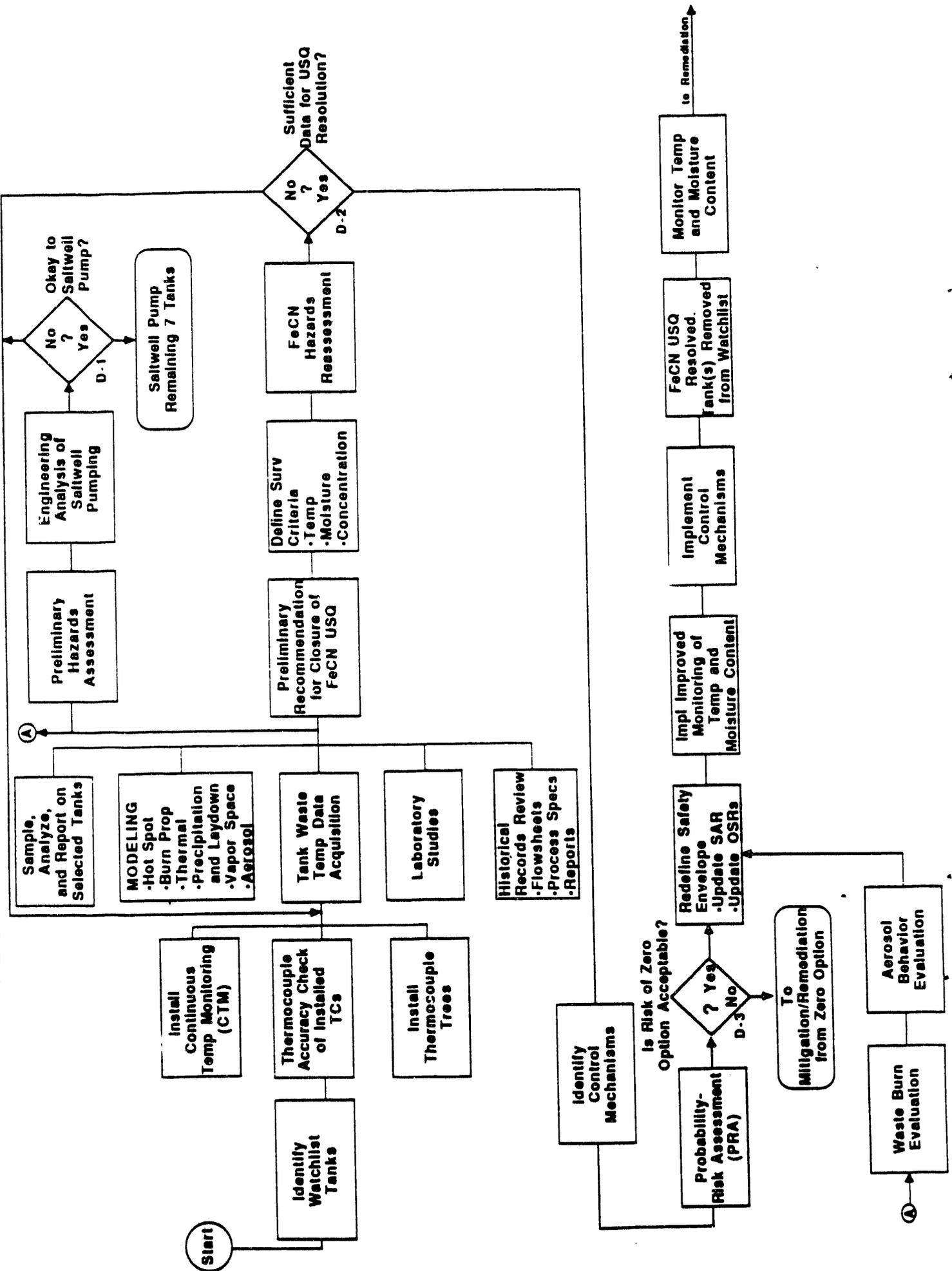
Surveillance and Controls: (Continued)

- **Concentration of waste will be important but not easy to control**
 - **3 flowsheets were used:**
 - **Laydown of the precipitate in the tanks could be important**
 - **May be a problem for a small number of tanks**
 - **Statistical confidence in core sample data**

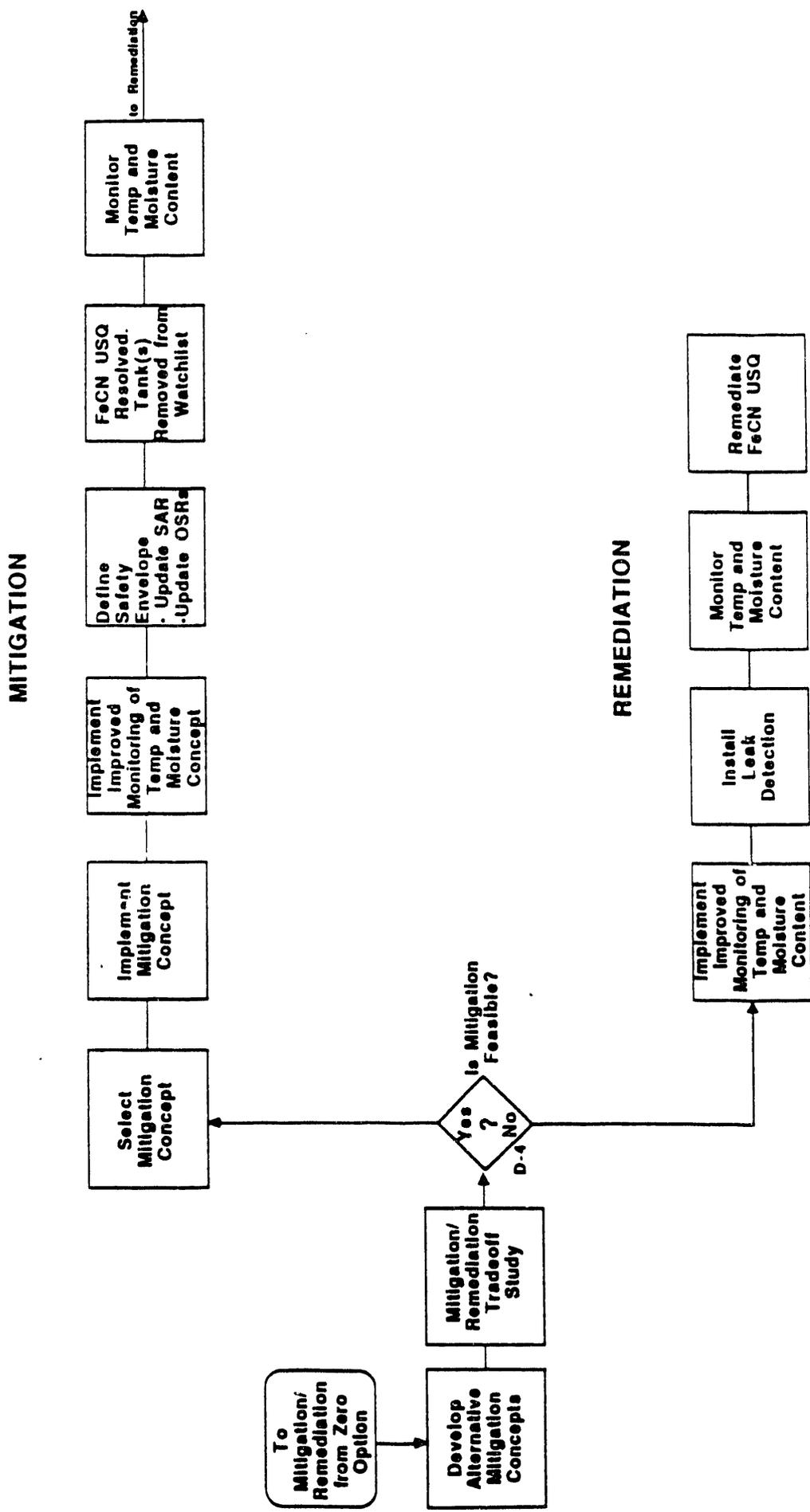
SCIENCE PANEL HELP

- **Modeling**
 - Laydown of the ferrocyanide precipitate: Was it uniform or could mounding have occurred?
 - Settling of particulates other than ferrocyanide material; are the ferrocyanide layers in a given tank homogeneous?
- **Instrumentation**
 - Moisture monitoring
 - Temperature monitoring
- **Examine logic for closure of Unreviewed Safety Question**

FERROCYANIDE ZERO OPTION DECISION LOGIC



FERROCYANIDE MITIGATION/REMEDIATION DECISION LOGIC



Appendix O

Letters from the Executive Committee

Contents

Letter to John L. Deichman Summary of Results from Tank Waste Science Panel Meeting	0.1
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Letter to John L. Deichman Comments on Gas Generation Work at WHC and PNL	0.17

December 3, 1991



Pacific Northwest Laboratories
Battelle Boulevard
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Telephone (509) 375-2550

Mr. John L. Deichman
Manager Tank Safety Project
Westinghouse Hanford Company
PO Box 1970
Richland, WA 99352

Dear John:

**SUMMARY OF RESULTS FROM THE TANK WASTE SCIENCE PANEL MEETING,
NOVEMBER 11-13, 1991, PASCO AND RICHLAND, WASHINGTON**

The sixth meeting of the Tank Waste Science Panel was held November 11-13, 1991 at the Red Lion Inn, Pasco and on the Washington State University - Tri City Campus, Richland. A brief summary of the meeting is given below.

HYDROGEN-GENERATING WASTES

- The work by Dan Reynolds in understanding the composition of the gases being released from Tank 241-SY-101 is a real step forward. This composition should be used to benchmark the results from the experiments being performed in the program. The composition derived by Dan is

<u>COMPONENT</u>	<u>VOLUME %</u>
H ₂	36
N ₂ O	28.5
N ₂	27
H ₂ O	4
NH ₃	4
Other	0.5

Mr. John L. Deichman

December 3, 1991

Page 2

- The Science Panel members were disappointed that a thorough report on the chemical analyses of the waste in Tank 241-SY-101 was not presented.
- The Science Panel members were concerned that the results from the gas generation studies with samples from the tank will yield results that will be reliable so that a comparison can be made with the results from the other studies. A flow-through apparatus similar to the one being used at Savannah River Site may be appropriate. Similarly, it is suggested that the same apparatus be used at Georgia Institute of Technology.
- Results from Dan Hertings gas generation studies indicate that the N_2O/H_2 ratio in the gases evolving from glycolate-containing simulated wastes more closely approximates the ratios observed in the gases from Tank 241-SY-101.
- Contact angles measured for gas bubbles grown on surfaces treated with simulated wastes with and without organics present suggest that the surfaces of the solid particles in the actual waste are slightly hydrophobic. This effect allows the bubbles to stick to the surface and may explain the origin of the crust and part of the retention mechanism for the gases in the nonconvecting layer.
- After preirradiation, the thermal generation of gases from simulated waste is increased substantially. This suggests that some product of radiolysis is long lived at room temperature and decomposes at test temperatures of 60°C. This important effect needs to be pursued. The identification of the active species in the preirradiated experiments needs to be identified.
- When formaldehyde containing only hydrogen, i.e. H_2CO , is mixed with D_2O/OD^- results indicate that only H_2 gas is released. If formaldehyde is the key species in the generation of H_2 , then these data suggest that the both hydrogen atoms originate from the formaldehyde rather than one from the formaldehyde and one from water. Formaldehyde is a product of the radiolysis of EDTA and HEDTA. For the waste in Tank 241-SY-101, other sources of H_2 are also possible.
- A fourteen step mechanism was proposed to explain the sources of H_2 , N_2O , N_2 , and NH_3 . Experiments are underway to verify these steps in the mechanism.
- An analysis of the organics in the crust samples has identified only 10% to 20% of the organics present. Since the thrust has been to identify the chelators, the analyses have been tailored to quantitate these. In the spectra for the organics in the crust samples, EDTA and several decomposition products have been identified. One product is MAIDA (methylamminoimmidodiacetic acid) is a product of the sample preparation, but is also found in the sample. The exact identification of

this species is ambiguous and may be changed when further tests are performed.

- The movement in the waste during a release event can be simulated using a system in which the viscosity is a function of the particle packing density. This mechanism may or may not be the mechanism operative in the tank. A material with more strength may be needed to explain more closely the actual waste behavior.
- The "gob" theory has been used to explain several of the observations of waste behavior. In particular, there is evidence from the decay of the waste height that the material that rose from the bottom of the tank during a release contains a significant amount of unreleased gas. This gas compresses upon descent in the tank and yields a sudden and more rapid waste height decrease about 10 days after the main release. The "gob" theory also explains why the heat content of the nonconvective layer recovers more rapidly than anticipated. It was also suggested that the nonconvective layer may be as much as 30% void volume and that only about 50% of the gas is released in the most energetic event.

FERROCYANIDE WASTES

- Ferrocyanide precipitates have been generated in the laboratory using the process flow sheets as a guide. These materials have been partly characterized and their decomposition studied. Additional information could have been discussed, but the principal investigator was not present.
- Information on the studies being carried out at WHC was not available because the principal investigator was not available.

REMEDIATION AND MITIGATION REPORTS

- The general tone of these reports needs to be changed to highlight the preliminary nature of the studies. More expertise needs to be brought to bear on the concepts before the list can be finalized and the top candidates selected.

EXECUTIVE SESSION

- Several letters will be written to suggest changes in the following areas:
 - Availability of core analyses data
 - Availability of gas analyses data

Mr. John L. Deichman
December 3, 1991
Page 4

- Focus in some of the experimental programs
- Experimental apparatus
- Emphasis on the organics being analyzed

If you have questions concerning the information discussed here, please contact me.

Sincerely,



Denis Strachan
Executive Secretary
Tank Waste Science Panel

cc: SG Agnew
RT Allemann
EC Ashby
H Babad
NE Bibler
SA Bryan
LL Burger
TM Burke
TH Dunning, Jr.
KA Gasper
RT Hallen
DL Herting
EP Horwitz
BM Johnson, Jr.
GD Johnson
WG Klemperer
MR Kreiter
DK Lemon
D Meisel
GB Mellinger
LG Morgan
LR Pederson
DA Reynolds
GA Russell
DD Siemer
WW Schulz
WJ Thomson
DS Trent
J Tseng
GB Wallis
File/LB



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January 17, 1992

Dr. Harry Harmon, Vice-President
Waste Tank Safety Operations/Remediation
Westinghouse Hanford Company
PO Box 1970
Richland, WA 99352

Dear Dr. Harmon:

RECOMMENDATION FROM THE TANK WASTE SCIENCE PANEL

After a rather intense week at the Tank Waste Science Panel meeting, November 11-13, 1991, listening to investigators present and discuss their results on Tank 101-SY and ferrocyanide waste tank issues, it is apparent that much progress has been made in the past year in understanding the relevant phenomena. We want to compliment both the engineers who monitor the waste tanks and the scientific staff involved in the research efforts on their progress.

The Tank Waste Science Panel members have a number of recommendations that will be relayed to John Deichman's Program Office and to the various investigators at Hanford and elsewhere. But, there are two issues concerning Tank 101-SY about which we feel strongly enough to communicate them directly to you. These involve aspects of the core sample analyses and the need to take an in-tank sample of the gas generated.

CORE SAMPLE ANALYSIS

For the past year, the scientific investigators have been using a synthetic waste composition which may or may not be close to that of the actual waste in Tank 101-SY. To make the next large step in the scientific work, it is imperative that the knowledge gained from the analyses of the core samples be made available to all team members so that, if needed, the information could be incorporated into the development of a new version of the synthetic waste.

One of the most critical information areas is the speciation (i.e., type and concentration) of the organic compounds in Tank 101-SY. Currently, investigators are conducting experiments with simulated waste containing organic compounds believed or known to be present when the waste was first generated. These compounds are not necessarily those currently in the tank.

When the analytical results for the waste in Tank 107-AN (Lokken, et al., 1986) are compared to the results presented to the Tank Waste Science Panel in our November,

Dr. Harry Harmon
January 17, 1992
Page 2

1991 meeting (cf. attachment), it appears that the ability to analyze for various organic compounds has eroded over the past five years! The analytical group at Pacific Northwest Laboratory was directed by Westinghouse Hanford Company staff and the Science Panel members to determine the concentration of organic chelators in Tank 101-SY. However, it is clear from the results of our other studies that this should no longer be the only directive. Adjustments need to be made in our strategy based on the results being obtained in the other parts of the program. To this end, there is reason to believe that glycolate, formaldehyde, and formate may be among the organic species key to the production of hydrogen. It appears that present analytical methods will not be able to detect or quantify low molecular weight organic materials. It is imperative that analytical methods capable of determining the presence and concentration of key low molecular weight organics be devised and applied to the problem at hand.

It also appears, with the current understanding of the waste in Tank 101-SY, that analyses of organic materials in the "crust" are much less important than previously thought. Identifying and quantifying the organic materials in the convecting and nonconvecting layers are of much greater importance. Experience gained in analyzing the solid crust samples is not lost since the nonconvective layer is about 85 wt% solids.

The PNL staff member who presented the results of the analysis of Tank 101-SY samples for organic materials stated that availability of a high resolution mass spectrometer would make identification and quantification of most organic material in Tank 101-SY much easier and less ambiguous. He indicated that the process to obtain this mass spectrometer is underway. We hope you will facilitate this effort by making sure that capital funds are readily available and that your staff will do all that is necessary to acquire this important piece of analytical equipment.

***IN SITU* GAS SAMPLES**

The uncertainties related to the composition of the gas vented by sampling at the vent header show that a better method needs to be devised to analyze gases originating in the tank. In the case of grab samples, the sample size should be large enough to yield an unambiguous analytical result. Although there is great reluctance on the part of Westinghouse Hanford Company tank farm managers to further instrument Tank 101-SY, information from such new instrumentation is needed if we are to develop an adequate understanding of the chemistry and physics taking place in Tank 101-SY. The Tank Farm managers should recognize this need and be encouraged to work as part of the research team over the next two years or so to obtain the needed information.

In addition to *in situ* measurements of the gases, it is becoming very clear that to support the remediation and mitigation efforts, *in situ* measurements of key physical properties are also needed. Currently, a waste simulant is being used that approximates the actual

Dr. Harry Harmon

January 17, 1992

Page 3

waste chemistry. However, the correlation between the actual waste physical properties and the physical properties of the waste simulant has not been verified. Without this verification, it may be very difficult to support a mitigation/remediation strategy based on results from the simulated waste.

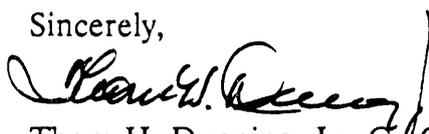
SUMMARY

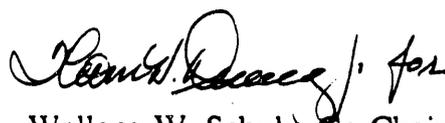
In summary, the Tank Waste Science Panel makes the following recommendations:

- 1) Timely information from analyses of core and off gas should be provided to the Tank Waste Science Panel and to other involved personnel. Such information should include the results of analyses for inorganics, semi-volatiles, organic materials, and gases, both from cryogenic samples and on-line measurements.
- 2) The analytical capabilities for identifying and quantifying organic materials should be upgraded to the current state-of-the-art.
- 3) Efforts to identify organic compounds should be concentrated on core samples and not on crust samples.
- 4) Glycolate, formaldehyde, and formate should be added to the list of key important organic species to be analyzed.
- 5) Establish the proper communication channel between the people doing the analyses and the experimenters trying to understand relevant phenomena. Provide flexibility on both parts to make changes as needed.
- 6) Capability for *in situ* sampling of the gas generated in Tank 101-SY and key physical properties of the waste should be put in place as soon as possible.
- 7) The tank farm managers and their staff should be encouraged to join in the research effort to facilitate quicker resolution of the gas generation problem in Tank 101-SY.

If you have questions concerning our recommendations, please contact one of us or Denis Strachan, Executive Secretary to the Tank Waste Science Panel.

Sincerely,


Thom H. Dunning, Jr., Co-Chairman
Tank Waste Science Panel


Wallace W. Schulz, Co-Chairman
Tank Waste Science Panel



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January 17, 1992

Mr. John L. Deichman
Westinghouse Hanford Company
P.O. Box 1970, MS R2-31
Richland, WA 99352

Dear John:

A portion of the recent (November 11-13, 1991) meeting of the Tank Waste Science Panel in Richland, Washington was devoted to review of the present status of bench-scale tests to synthesize and characterize various ferrocyanides and ferricyanides which might be present in one or more of the 24 Ferrocyanide Waste Tanks. We thank Dr. Lee Burger for providing us this update. We also thank Mr. Robert Cash for providing us the gist of the logic diagrams and other information from the forthcoming "white paper" on Ferrocyanide Waste Tanks. Also, as you know, some members of the Tank Waste Science Panel attended part of the Technical Advisory Committee on November 14, 1991 when Mr. Cash again reviewed various facets of ferrocyanide waste research studies and mitigation/remediation plans.

From the information available to us and from our Executive Session meeting, the Tank Waste Science Panel has three major concerns and recommendations we want to bring to the attention of you and your staff.

**CONCERN 1 NEED FOR ACCELERATED CHARACTERIZATION OF THE
EXPLOSIVE PROPERTIES OF ACTUAL FERROCYANIDE TANK
WASTES**

The Tank Waste Science Panel has already clearly stated (PNL-7822, page 34) that the overriding and primary scientific issue concerning Hanford Ferrocyanide Tank Wastes is the need to determine the composition and properties of actual tank wastes. We believe that you, your staff, and, indeed, everyone concerned with the continued safe mitigation/remediation of the Ferrocyanide tanks wastes concur with our assessment. Indeed, as you clearly stated at the Technical Advisory Panel meeting, the entire issue of the Ferrocyanide Tank Waste mitigation can never be entirely closed without satisfactory and definitive characterization data.

The Tank Waste Science Panel is well aware that Westinghouse Hanford Company plans to eventually sample and characterize wastes in all of the 24 Ferrocyanide tanks. We also are well aware of the many and real constraints that severely limit the pace at which all 24 of the Ferrocyanide tanks can be sampled and characterized, namely:

Mr. John L. Deichman
January 17, 1992
Page 2

- limited sampling equipment (1 or 2 sample trucks),
- limited hot cell space,
- limited funding for sampling and analyses,
- conflict with Environmental Restoration Division tank sampling schedules and characterization information,
- and others.

Because of these constraints, the Tank Waste Science Panel asks that you and your staff consider responding favorably to the following recommendation as a way of expediting acquisition of highly-useful and statistically-significant characterization data for one important Ferrocyanide waste tank.

RECOMMENDATION 1 Conduct an engineering study to devise and evaluate a plan for statistically-significant accelerated determination of the explosive properties of waste in one ferrocyanide waste tank.

What the Tank Waste Science Panel has in mind is:

- Choose a tank to sample based upon quantity of ferrocyanide waste put in the tank; upon the tank history after deposition of the ferrocyanide waste, i.e., whether or not the ferrocyanide waste likely came in contact with highly alkaline liquids; and the number of available risers for taking core samples. Choose a tank most likely to still contain ferrocyanide waste which has not been hydrolyzed; a tank into which a large quantity of ferrocyanide waste was originally deposited; and which has a large number of accessible risers for sampling.
- Take duplicate (or more) core samples from every available riser in the chosen tank.
- Consider (see Item 4 below) drilling more risers in the tank to take additional core samples from different locations in the tank.
- Characterize material in the bottom (of the tank) segment (perhaps bottom 2 segments) only for explosive properties (i.e., DSC and TGA analyses).
- Utilize guidance of statisticians throughout to determine number of core samples, number and location of samples from core segments, etc., to state, at various

Mr. John L. Deichman
January 17, 1992
Page 3

confidence levels (e.g., 50%, 75%, 90%, 95%), whether or not the waste in the chosen tank exhibits any explosive behavior.

The Tank Waste Science Panel views this sampling and characterization approach as the most efficient (most rapid and least costly) way of obtaining defensible and useful information about actual ferrocyanide wastes. For example, consider two possible outcomes:

- Material in one or more sample segments is explosive.
- None of the material in any segment analyzed is explosive.

In the first case, we will know that at least one tank contains some explosive material; we will also have an idea of how much energy would be released if the material did explode. Mitigation and remediation strategies can be planned and executed with much more assurance that they are correct and adequate. A conservative assumption in this case also is that all of the 24 tanks contain at least some explosive material.

Now suppose that the second case prevails, i.e., no explosive material is found in any of the samples. These data are not sufficient to state unequivocally that other Ferrocyanide Waste Tanks do not contain some explosive material. But, if no explosive material were found in the waste from the tank most likely to contain such material, the safety concerns of everyone concerned (Westinghouse Hanford Co., DOE, the Defense Nuclear Facilities Board, State of Washington, etc.) would all be greatly reduced. And, sampling of the other ferrocyanide tanks could proceed on a less intense basis.

CONCERN 2 NEED FOR A DEFINITIVE PLAN FOR COMPLETING BENCH-SCALE TESTS WITH SIMULATED FERROCYANIDE WASTES

Bench-scale tests to synthesize many different ferrocyanide and ferricyanide compounds and to characterize their reaction with solid nitrate/nitrite compounds have been underway off and on since 1984. Much has been learned, and the Tank Waste Science Panel commends Dr. Burger and Dr. R. Scheele for the excellence of their science.

To date, however, no one has defined for the Tank Waste Science Panel exactly what further tests with simulated ferrocyanide tank wastes are planned, specific objectives and information to be gained from such tests, and the approximate date when all simulated waste tests will be completed. The Tank Waste Science Panel had no desire, whatsoever, to terminate any useful testing with simulated wastes, quite the contrary (see, for example, Concern 1 and Recommendation 1). But, the Tank Waste Science Panel cannot adequately and completely provide guidance to further research studies without

Mr. John L. Deichman
January 17, 1992
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some idea of their scope and objectives. Therefore, the Tank Waste Science Panel recommends:

RECOMMENDATION 2 Prepare a plan which addresses the scope, objectives, and estimated completion dates for further tests and studies with simulated ferrocyanide tank waste.

The Tank Waste Science Panel asks that such a plan, along with the other work we understand is taking place, be presented to them on or before the occasion of their next meeting, which should occur in the February to April, 1992 time frame.

**CONCERN 3 NEED FOR KINETIC (RATE) DATA FOR REACTIONS OF
FERROCYANIDES WITH NITRATES AND NITRITES**

The Tank Waste Science Panel is concerned that the present bench-scale tests do not address the important question of the rate at which various simulated ferrocyanide and ferricyanide compounds react with nitrites and nitrates as a function of temperature. Availability of reliable reaction rate data would enable prediction, with a high degree of confidence, of whether possible reactions will produce heat at a faster rate than it can be removed. We do not believe that the present TTX tests provide such rate data since the results of such tests are completely dependent upon the heat transfer rates associated with the particular test apparatus.

RECOMMENDATION 3 Devise and perform definitive tests with simulated ferrocyanide wastes to obtain reliable reaction rate data.

We appreciate the consideration you and your staff will give to the concerns and recommendations of the Tank Waste Science Panel concerning ferrocyanide wastes. Of course, we are always available to discuss further our concerns and recommendations.

Sincerely,



Thom H. Dunning, Jr., Co-Chairman
Tank Waste Science Panel



Wallace W. Schulz, Co-Chairman
Tank Waste Science Panel



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January 17, 1992

Dr. Eugene C. Ashby
Department of Chemistry
Georgia Institute of Technology
Atlanta, GA 30332

Dear Gene:

All of us on the Tank Waste Science Panel were very favorably impressed by your presentations, especially the one on Wednesday, November 13, at our recent meeting in Richland. It is clear that you have assembled a dedicated and talented research team at Georgia Tech. It is also evident that you and your team made good progress in the interim between our July and November meetings in identifying and elucidating the mechanism of gas generation in simulated Tank 101-SY waste. The Georgia Tech results to date confirm earlier observations and provide valuable new information about the source of gases generated in Tank 101-SY.

The Panel believes, as you do, that it is of continuing and great importance to identify the species and mechanisms responsible for the chemical production of gases in simulated Tank 101-SY waste. This understanding is critical to the evaluation of proposed mitigation and/or remediation measures for Tank 101-SY.

We spent considerable time at our Executive Session on November 12, 1991, discussing the results and direction of the Georgia Tech program with simulated Tank 101-SY waste. Two important points and recommendations emerged from our discussions which we bring to your attention in this letter.

RECOMMENDATION 1

We recommend that you and your group discontinue, for the near-term, experiments in which effects of addition of certain metal ions are added to simulated Tank 101-SY waste or of irradiation of simulated waste with sonic energy. The results that you have obtained to date are interesting but too incomplete to draw definite conclusions. The Panel feels that available time and financial resources should be focused on the immediate problem of identifying relevant gas production species and mechanisms. The need and/or desirability of further experimental work involving sonic energy and/or effects of added metal ions should be reconsidered at a later time.

Dr. Eugene C. Ashby
January 17, 1992
Page 2

RECOMMENDATION 2

The electron transfer mechanism that you have proposed and your group is diligently testing came in for much discussion at our Executive Session. Understandably at this point, some members of the Tank Waste Science Panel are openly skeptical of all or at least some features of the proposed reaction mechanism. We recognize and appreciate the great energy and time required in devising the mechanism which you proposed. As you noted, the proposed mechanism takes into account all available and relevant experimental data, and your group is hard at work performing experimental work to confirm (or refute) the mechanism. We believe you should continue on the course you have laid out.

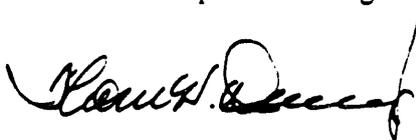
But, we also ask that you consider whether alternative pathways/mechanisms can be proposed to explain the experimental observations. Such consideration, we feel, should involve not only the Georgia Tech group, but also some of your knowledgeable colleagues at other academic institutions. This exercise is needed not only to reinforce confidence in the proposed electron transfer pathway, but also to give us all a "heads up" in case future evidence does not support all or certain parts of the currently proposed mechanism.

RECOMMENDATION 3

In our Executive Session, there was also considerable discussion about the gas generation data you presented. We could understand why, when the first time these data were presented, the amount of gas produced was not corrected for temperature and pressure. However, none of the gas generation data have since been corrected. In the future, we urge you to make these corrections before reporting them. Making these corrections should be a relatively simple task in this age of computers.

Of course, as always, please call either one of us or Denis if we can provide further insight into our recommendations.

All our best personal regards to you.



Thom H. Dunning, Jr., Co-Chairman
Tank Waste Science Panel



Wallace W. Schulz, Co-Chairman
Tank Waste Science Panel

January 17, 1992



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Dr. Dan Meisel
Chemistry Department
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Dear Dan:

All of us on the Tank Waste Science Panel were very impressed by your excellent presentations at our November 11-13, 1991 meeting in Richland, Washington. We were even more impressed with the outstanding work performed by the Argonne National Laboratory group under your direction. It is clear that the Argonne group, in a relatively short time, has obtained much valuable data and is well on its way to elucidating all of the important features of radiation-induced processes which lead to the production of H_2 and N_2O in Tank 101-SY waste.

We greatly appreciate your outline and schedule of further laboratory work. All the tasks you told us about and have scheduled are certainly important and relevant.

But, the Panel is concerned that the schedule presented in November did not include any further studies of the effects of pre-irradiation on subsequent thermal generation of gases from simulated wastes. We believe that the phenomenon, because of its potential and poorly understood impact upon any physical mitigation methods applied to Tank 101-SY, merits considerable more investigation. If you have not already done so, the Panel strongly suggests that you request a change in work scope through Westinghouse Hanford Company so that you can give priority attention to the pre-irradiation phenomenon. A key task is to identify the intermediate responsible for the production of gases in the pre-irradiated waste. If necessary, you should enlist the aid of Gene Ashby and his group at Georgia Tech or the group at PNL in identifying the relevant intermediate.

Our best wishes and regards,

A handwritten signature in black ink, appearing to read "Thom H. Dunning, Jr." with a stylized flourish at the end.

Thom H. Dunning, Jr., Co-Chairman
Tank Waste Science Panel

A handwritten signature in black ink, appearing to read "Wallace W. Schulz" with a stylized flourish at the end.

Wallace W. Schulz, Co-Chairman
Tank Waste Science Panel

February 19, 1992



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Mr. John L. Deichman, Manager
Tank Waste Safety Program
Westinghouse Hanford Company
P.O. Box 1970, MS R2-31
Richland, WA 99352

Dear John:

At the meeting of the Tank Waste Science Panel last November in Pasco, Washington, we heard D. A. Reynolds, S. A. Bryant, and L. R. Pederson make presentations on the work being performed at WHC and PNL concerning possible gas generation reactions in Tank 101-SY. Dan Reynolds reported the work that D. L. Herting is doing in preparation to measuring gas production from core samples from Tank 101-SY. Sam Bryant and Larry Pederson discussed their work (Task 05 of the PNL Hydrogen Safety Project) on the chemo-physical studies of gas retention on sludges in Tank 101-SY and their program entitled Integrated Gas Generation studies. As a result of these presentations, the Science Panel has several comments.

The Science Panel feels that the tests by Dan Herting on gas generation from actual radioactive samples of Tank 101-SY cores are of paramount importance. Such tests should give reliable and accurate measurements of the composition of the gas generated in Tank 101-SY. We understand that these tests have now already begun and are being conducted in the batch mode with gas samples being taken by the evacuated bulb technique. We anxiously await these initial data. The Panel feels that Dan is to be commended for his initiative and perseverance in getting these important tests started. We were, however, disappointed that Dan was unable to attend our meeting in Pasco. The Science Panel does have a recommendation concerning Dan's tests. We recommend that Dan investigate the possibility of using a flow-through apparatus as a backup system if the batch apparatus does not produce satisfactory data. A flow-through apparatus might yield more reliable results especially in a hot cell. This apparatus allows a gas sample to be taken automatically as well as analyzed automatically (by gas chromatography). Beginning last September, Savannah River Laboratory has used such an apparatus in a hot cell environment. Their apparatus was used to measure H_2 , N_2O , and CO_2 produced by the reaction at about $100^\circ C$ between formic acid and actual radioactive Savannah River Site sludges. Hydrogen results from decomposition of formic acid catalyzed by the noble metal fission products in the waste. Gas samples were automatically taken and analyzed every five minutes. Argon was used as the carrier gas. The sensitivity for H_2 was 0.01% or better. The Science Panel recommends that Dan contact Ned Bibler (FTS-239-2313) at Savannah River Laboratory to determine if this apparatus could be useful for his tests.

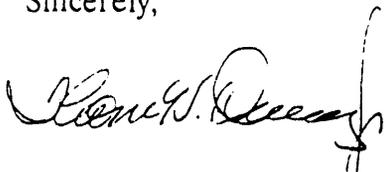
Mr. John L. Deichman
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The Panel feels that the work of Sam Bryant and Larry Pederson is progressing well, but several comments are in order:

- Especially interesting are the results concerning the effect of HEDTA and EDTA on bubble contact angles. The Panel would like to see these experiments repeated using irradiated solutions of EDTA and HEDTA. Larry and Sam presented preliminary results of a test designed to measure the transport of N_2O through water. From the data presented, it appears that gas was simply dissolving in the aqueous phase rather than being transported through it. The Panel feels that these tests need to be reassessed and if the goal is to measure diffusion, perhaps this is not the correct apparatus to use.
- It appears that the radiolysis experiments at PNL are in many cases simply duplicating the efforts at ANL. The Panel recommends that the PNL program be examined so that excess duplication is avoided.
- The steel corrosion results are interesting. It appears that H_2 can be a product of iron corrosion under certain conditions and we encourage the continuation of these tests. It is important however, to emphasize that these tests were performed under conditions where steel corrosion would be accelerated and do not necessarily indicate actual corrosion rates in the tanks.

The Panel hopes the comments are helpful. Please accept our apologies for transmitting them to you so long after the meeting.

Sincerely,



T. H. Dunning, Co-Chairman
Tank Waste Science Panel



W. W. Schulz, Co-Chairman
Tank Waste Science Panel

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