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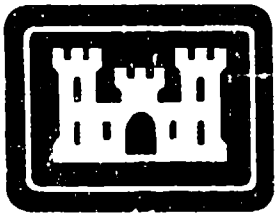

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FINAL REPORT

Removal of DNT from Wastewaters at Radford Army Ammunition Plant

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2,4-Dinitrotoluene (DNT), a chemical used in the manufacture of single-base propellants, is a suspected carcinogen and has also been linked to heart disease by some studies. In processing propellants containing this ingredient at Radford Army Ammunition Plant (RAAP, Radford, VA), wastewater is generated containing various concentrations of DNT. This wastewater requires abatement prior to discharge into the New River. At present, a central biological wastewater treatment plant (BWTP) is operated at RAAP for treating wastewaters. Though the Virginia State Water Control Board has not established limits on DNT discharge, monitoring is required; DNT content is discharged wastewaters must be reported semi-monthly. Additionally, in the March 29, 1990 Federal Register, 2,4-DNT was listed as a constituent hazardous organic chemical.

This project was tasked with the following: performance of a literature review to identify technologies available for both DNT destruction in wastewaters and DNT removal methods;
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based on the literature review, selection of the most promising technologies for evaluation in the laboratory to determine their removal efficiency; and bench-scale evaluations of one or more optimum technologies to quantify DNT destruction/removal efficiency and to select the best available and most cost effective technology for application at RAAP. Additionally, research was to be performed to evaluate bioaccumulation and determine if DNT was toxic to microorganisms utilized in wastewater treatment.

It was concluded that GAC treatment should be used as a means to achieve DNT discharge goals in the short-term. This technology is developed, reliable, and readily available. Both UV/ozonation and biological degradation are DNT abatement technologies that warrant further study. Pilot-scale UV/ozonation studies are recommended to establish optimal conditions and assess economics. Additionally further research on biological degradation of DNT is needed to identify biotransformation products, to further develop the technology and thereby reduce risks of implementation.

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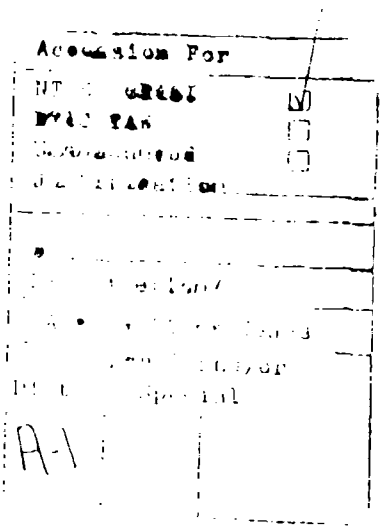

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INTRODUCTION

2,4-Dinitrotoluene (DNT), a chemical used in the manufacture of single-base propellants, is a suspected carcinogen and has also been linked to heart disease by some studies. In processing propellants containing this ingredient at Radford Army Ammunition Plant (RAAP, Radford, VA), wastewater is generated containing various concentrations of DNT. This wastewater requires abatement prior to discharge into the New River. At present, a central biological wastewater treatment plant (BWTP) is operated at RAAP for treating wastewaters from propellant and nitrate ester manufacturing processes. The nitrate ester wastewaters are chemically pretreated prior to being combined with the propellant wastewater, then treated biologically. Though the Virginia State Water Control Board has not established limits on DNT discharge, monitoring is required; DNT content in discharged wastewaters must be reported semi-monthly. Additionally, in the March 29, 1990 Federal Register, 2,4-DNT was listed as a constituent hazardous organic chemical. The purpose of this engineering study was to characterize the sources of DNT that feed into the wastewater collection system and to identify and develop the technology for removal/destruction of DNT from these wastewaters.

During 1989-1990 a survey of the wastewater collection system was conducted to identify and characterize all wastewater streams containing DNT. DNT is a negative rate and energy modifier which is used mostly in cannon propellants. Additionally, it is used as a surface inhibitor for cannon propellants. The current formulations being processed contain roughly 3-10% DNT by weight. The primary DNT sources were single-base manufacturing operations such as the water dry (WD), solvent recovery (SR), wet screening (WS), and coating operations (CO). Analysis of the effluent stream from the BWTP indicated an intermittent release of low concentrations of DNT. Further study indicated that treatment of the WD and the WS wastewater alone may be sufficient to eliminate discharge of DNT from the BWTP. Additionally, little or no detectable quantities of DNT were found in the sludge or rotating biological contactor (RBC) biomass.

This project was tasked with the following: performance of a literature review to identify technologies available for both DNT destruction in wastewaters and DNT removal methods; based on the literature review, selection of the most promising technologies for evaluation in the laboratory to determine their removal efficiency; and bench-scale evaluations of one or more optimum technologies to quantify DNT destruction/removal efficiency and to select the best available and most cost effective technology for application at RAAP. Additionally, research was to be performed to evaluate bioaccumulation and determine if DNT was toxic to microorganisms utilized in wastewater treatment.

CHARACTERIZATION

Figure 1 contains a generalized process flow chart of single-base manufacturing operations. Nitrocellulose (NC) is first dewatered by centrifugal action (wringer house) and solvent extraction (dehydration building). Procured DNT is sized by screening and weighed at the DNT screen house for mixing with the

NC and other ingredients at the mix houses. After mixing is performed, the material is pressed into blocks which are extruded through screens and dies to remove unplasticized material (block and macaroni presses). The material is then extruded through dies and cut into the desired configuration (press and cutting house). Inert gas is utilized to extract and recover processing solvents (SR) followed by exposure to water and heat to further reduce the solvent content of the propellant (WD). WS is then performed to properly size the propellant and air (air dry) is utilized to reduce the moisture content of the propellant. The remaining operations involve packout of the material. Additionally, some propellants require a coating of DNT which is performed at the CO.

There are four major propellant formulations produced at RAAP containing DNT. These single-base solvent propellants which contain 3-10% DNT are M1, M6, M14, and LKL. In addition, IMR propellants receive a DNT ballistic inhibitor coating. The locations where DNT could enter the wastewater system from the processing steps are also shown in figure 1. There are six process wastewater streams, but only the following four contribute significant quantities of wastewater containing DNT: SR (cool down wash water and motive water), WD (process water, motive water, leak and overflow water), motive water for the WS, and the DNT CO water. All buildings involved receive a dry cleanup before wash-down which effectively prevents DNT from entering the wash-down water. The air dry (AD) buildings require cleaning approximately once a month and are dry cleaned prior to wash-down.

M1, M6, and LKL propellants were the primary DNT-containing propellants being manufactured during this evaluation. Therefore, the majority of the water samples were taken while processing these three propellants. Characterization of the DNT-containing waste streams was accomplished by collecting samples and analyzing from the SR, WD, WS, and CO. Grab samples were taken when the other single-base propellant formulations were being processed. Flow rates were either measured or estimated.

Process Flow Sources

In SR and WD operations, water used to remove solvents from propellants during processing becomes contaminated with other propellant ingredients such as DNT. The SR buildings contain five tanks per building (generally four utilized) which hold ~10,000 lb of green (solvent rich) propellant. After the propellant is exposed to heated inert gas to remove and recover the solvents, the propellant is covered with water (1,250 gal./building) at the end of the cycle to remove the surface solvents and to reduce the electrostatic potential. Water (3,790 gal./building) is then used to move the propellant from the tanks into transfer buggies. These waters, ~5,040 gal./SR building, become contaminated with DNT, ethyl ether (ether), and ethyl alcohol (alcohol).

At the WD operation, residual amounts of processing solvents are removed by exposing the propellant to hot water. Approximately 40,000 lb of propellant in one tank is covered with water and heated to 65°C for 4 to 18 days depending on the propellant formulation and physical data. During the WD cycle, it is estimated that 7,000 gal. of process water is released from each WD tank during

draining and 3,320 gal. is required to discharge the propellant from the tanks to transport buggies (1,890 gal. for the wood tanks and 4,740 gal. for the fiberglass tanks). Additionally, it is estimated that the average WD tank leaks and overflows 6,820 gal./day. These leaks are caused by the aged wooden WD tanks which have not been replaced by fiberglass tanks. These wooden tanks have small cracks between the boards which permits water to leak; especially if the wood is allowed to dry.

The last major sources which produce DNT wastewaters are the WS and CO's. The WS house generates 40,000 gal./WD tank and the CO generates 300 gal. of coating water/1,000 lb of propellant (50,000 to 100,000 lb of DNT propellants coated/yr).

Clearly, the WD's contribute the larger quantity of DNT-containing wastewater and sampling was concentrated at the WD buildings. The results of WD wastewater sampling during a nine-day period are presented in table 1. These samples were collected at the end of the WD cycle during draining. As shown in table 1, samples were collected from the processing of two M1-type propellants; M67 and M724. The average DNT concentration in the wastewater for the M67 propellant was ~160 mg/L and 280 mg/L for M724. Chemical oxygen demand (COD) for the M67 was 2,100 mg/L O_2 versus 6,100 mg/L O_2 for the M724.

Additional WD sampling was performed over a six-month period (table 2). The propellant formulations produced during this period were M14, M6-155, and LKL 120-mm. Additional items were characterized such as COD, ether, alcohol, diphenylamine (DPA), dibutylphthalate (DBP), and N-nitrosodiphenylamine (NnDPA). NnDPA results when the stabilizer DPA is utilized by the propellant to react with NO_2. This occurs if the propellant is exposed to excessive heat during processing. M14 and M6 propellants produced the higher DNT concentrations (as high as 370 mg DNT/L) while LKL produced lower DNT concentration due to it containing a lower DNT concentration and longer treatment period. Solvents (total) were present at less than 1,000 mg/L and other contaminants were usually only a few mg/L. Generally; if it is assumed that each WD tank releases 7,000 gal. of 200 mg DNT/L of process water, 3,320 gal. of motive water (0 mg DNT/L), and the WD area releases 122,731 gal./day of leak/overflow water containing 6.4 mg DNT/L into the waste collection system; this results in roughly 8.3 kg of DNT/WD tank.

In addition to WD samples, samples were taken at the WS house, the cool down wash from a SR building, and IMR CO. The results are shown in table 3. The estimated release of DNT into the wastewater collection system for the SR's is 0.8 kg DNT/WD tank, 2.0 kg DNT/WD tank for the WS house, and 0.034 kg DNT/day for the CO.

Wastewater Collection System

Figure 2 represents a map (darkened buildings) of both active SR buildings (large rectangles) and WD (small rectangles). According to the map, only WD and WS building drainage could be intercepted at manhole (MH) 32 (see arrows on fig. 2). Additionally, all SR wastewater could be intercepted from MH 36. These MH's

were located and field-surveyed to confirm rim and invert elevations for the purpose of conducting a flow measurement study based on water depth measurements and the Manning formula. Automatic flow-proportional 24-h composite wastewater samplers and continuous recording flowmeters were utilized.

Table 4 contains the flow, COD, and concentration of various components of the wastewater at MH's 32, 34, and 36 in addition to the BWTP. Both 24-h composite and grab samples were collected. MH 36 was further divided by a grab sample to differentiate wastewater from six isolated SR's (MH 36A) and a wastewater from the propellant manufacturing areas (MH 36B). The flow rate from the SR's was 0.3 MGD; however, no SR's were discharged during the measurement period as is further confirmed by 0.54 mg DNT/L detected. (This may be due to SR condenser water discharging into the drainage system). MH 32 contains the water from nine WD's and two WS buildings with an average flow rate of 0.18 MGD and 6.4 mg DNT/L concentration from the composite sample (grab =75.8 mg DNT/L). Since the water discharge and DNT concentration from the WD's was known, MH 32 was measured during a period when no WD's or WD buildings were operated to determine the quantity of wastewater and DNT concentration from leaking and overflowing tanks.

In summary, utilizing the preceding data, a rough estimate of the sources of DNT for the BWTP can be generated with respect to one WD tank (table 5). These are: 0.8 kg from the SR's, 5.3 kg from the WD tank, 3.0 kg/day from leaks/overflows of the WD tanks, and 2.0 kg from the WS buildings. This would indicate that the SR's contribute 7%, the WD's 48%, the WD leaks/overflows 27%, and the WS buildings 18%. During a 307-day count, 308 WD tanks containing DNT propellants were discharged indicating that one WD tank containing DNT is discharged per day. This would indicate that 0.28 kg of DNT is released to the wastewater collection system per 1,000 lb of DNT-containing propellant manufactured.

If a treatment system were installed to intercept the wastewater at MH 32 and production restricted to processing all of the DNT propellants in the WD's that drain into MH 32, it is estimated that greater than 90% of the DNT influent load to the BWTP could be intercepted. Additionally, the average quantity of wastewater for treatment at MH 32 would be 0.18 MGD instead of 1.28 MGD at the BWTP and would be considerably easier to treat. If necessary, similar restrictions could be placed on the SR area so that SR wastewater could be collected at MH 36 and piped to the treatment installation for MH 32. If production increases the DNT coating operations, a basin should be constructed at the coating operations for collection of the coating and wash-down water (cooling water should be separated and treated normally). This wastewater can then be transported to the DNT treatment facility.

Biological Wastewater Treatment Plant

Composite samples (24-h) of the wastewater being processed through the BWTP were analyzed for DNT and COD. The high performance liquid chromatograph (HPLC) chromatograms were examined for the formation of biotransformation by-products. Figure 3 represents the wastewater flow through the BWTP. The wastewater is

pumped by a lift station to the aeration/equalization basin (aeration is provided along with nutrients to enhance biodegradation), new RBC's, old RBC's, and two clarifiers. (Note: The BWTP was previously expanded with the addition of a new set of RBC's.) Sludge is removed from the clarifiers to aerobic digesters, a thickener, and finally a filter press. Table 6 presents the DNT analysis results for BWTP raw composite influent, grab sample raw influent, grab sample new RBC influent, grab sample old RBC influent, and BWTP effluent. Table 7 presents the results for COD analysis at the same locations. Based on an average wastewater flow rate of 1.13 MGD during this sampling period with an average influent DNT concentration of 7.67 mg DNT/L, an average of 72.2 lb/day (32.75 kg/day) of DNT reached the BWTP and an average of 1.54 lb/day (0.70 kg/day) of DNT was discharged in the effluent. It was observed that an average of 62% of the DNT was removed in the aeration/equalization basin and 36% was removed in the RBC's. Additionally, these results indicate an average overall removal of 98%, with a maximum of 1.2 mg DNT/L discharged from the BWTP.

Analysis of the chromatograms (figs. 4 through 8) confirmed the gradual reduction of DNT. DNT had an average retention time of 4.4 min on these chromatograms and the representative peak in the chromatograms (figs. 4 through 8) decrease in size as the wastewater proceeds through the facility. Additionally, the HPLC chromatograms for DNT analysis were utilized to observe for DNT biotransformation products by observing peak patterns. The formation of a new peak, which could be a biotransformation by-product, was observed at ~3.37 min (figs. 5 through 8). Literature reports indicated a number of transformation by-products with one of the ultimate end products being 2,4-diaminotoluene (DAT).

In order to document the previous history of DNT discharged from the BWTP, the weekly effluent composite samples are plotted in figure 9. The sporadic high discharge levels were compared to production levels of DNT-containing propellants for this period. No correlations between the level of production of individual propellants and DNT discharge levels were noted.

Complete statistics, utilized obtaining a discharge permit for the BWTP, are contained in table 8. Effluent data concerning flow, pH, five-day biological oxygen demand (BOD_5), total suspended solids (TSS), COD, sulfates (SO_4), nitrogen (N), and DNT is represented by an average daily quantity on a monthly basis and summarized for the year. The effluent flow from the BWTP averaged 1.28 MGD with a maximum flow of 3.09 MGD. DNT effluent loading for the period averaged 1.65 kg/day with a maximum of 26.7 kg/day. The effluent contained an average of 0.264 mg/L with a maximum of 3.60 mg/L. This information indicates that if discharge limitations are imposed on the BWTP for DNT, some modification or improved treatment will be required.

Biomass samples taken from the RBC's and the filter press of the BWTP indicated no DNT accumulation. The samples were taken to ascertain the potential for DNT accumulation or other biological breakdown products in the biomass. The analysis was performed with either acetonitrile or methanol as the extraction solvent to further assure that DNT was not accumulating. Further studies conducted using sulfuric acid to digest the biomass prior to analysis also did not indicate significant accumulation.

LITERATURE REVIEW

A survey was conducted to identify technologies available for destruction of DNT in wastewaters and to identify DNT removal methods. The decomposition of DNT and its associated by-products from various treatment methodologies were also reviewed wherever available in the literature.

Technological Review

Approximately 60 articles were reviewed concerning biological, activated carbon, incineration, oxidation, reduction, and general wastewater treatment. Some articles contained little or no specific information relating to DNT; however, they either provided insight into treatment technologies for DNT or similar compounds as described below.

Biotransformation or Biodegradation

Sixteen articles contained information on biological destruction of DNT. All articles indicated biotransformation occurred with no evidence of aromatic ring destruction. (Limited information is available that indicates breakage of the aromatic ring and will be discussed at the end of this section.)[2,3] However, previous reports required the formation of a diphenol as a necessary prerequisite for degradation of the aromatic nucleus.[4] For the structurally similar compound TNT, it was reported there is no evidence for biological cleavage and degradation of the aromatic ring of TNT.[4] Stepwise reduction of the nitro groups by various organisms (mammalian, bacterial, and fungal) occurs through the nitroso and hydroxylamino to the amino. Various compounds identified were: 4-amino-2,6-dinitrotoluene (4A); 2,4-diamino-6-nitrotoluene (2,4DA); 2,2',6,6'-tetranitro- 4,4'-azoxytoluene (4,4'Az); 4-hydroxylamino-2,6- dinitrotoluene (4HA); 2-amino-4,6-dinitrotoluene (2A); 4,4',6,6'-tetranitro- 2,2'-azoxytoluene (2,2'Az); and 2,4,6-triaminotoluene (TAT).[4]

For DNT, the following microbial transformation compounds were identified: 2,4-diaminotoluene (2,4DAT); 2,6-diaminotoluene (2,6DAT), 2-amino-4-nitrotoluene (2A4NT); and 4-amino-2- nitrotoluene (4A2NT). The microorganisms *Veillonella alkalescens*, *Escherichia coli*, *Chostridium pasteurianum*, and pseudomonad FR2 was evaluated for the ability to degrade nitroaromatic compounds. These biological systems (both aerobic and anaerobic) demonstrated the ability to catalyze the reduction of at least one nitro group. The 4-nitro group was always reduced first.[4] Another article described a method for evaluating biotransformation using both anaerobic and aerobic microorganisms. DNT was biotransformed by both organisms; however, ring breakage could not be demonstrated. The anaerobic biotransformation products could not be identified.[5]

Effort involving activated sludge indicated that microbial transformation of 2,4-DNT occurred only under anaerobic conditions utilizing

activated sludge (no activity was observed under aerobic conditions). Products detected were: 2A4NT, 4A2NT, 2-nitroso-4-nitrotoluene (2NO4NT), and 4-nitroso-2-nitrotoluene (4NO2NT).[6]

An evaluation of the products from the microbial transformation of 2,4-DNT by *Mucrosporium* species (strain QM9651, NLABS Culture Collection of Fungi) identified: 2A4NT; 4A2NT; 2,2'-dinitro-4,4'-azoxytoluene; 4,4'-dinitro-2,2'-azoxytoluene and 4-acetamido-2-nitrotoluene. A third azoxy compound could not be identified. Again none of the compounds indicated ring breakage.[7] One-hundred and ninety fungi representing 98 genera were screened for the ability to transform 2,4,6-TNT and 2,4-DNT. One-hundred and eighty-three of the organisms were able to transform TNT while only five were able to transform DNT. The study concluded that the utilization of fungi to treat TNT wastewater appears unpromising in view of their failure to degrade TNT and DNT and the possibility that the amino transformation products are toxic.[8]

Microbial degradation was further evaluated using industrial seed comprised of four bacterial genera (*Acinetobacter*, *Alcaligenes*, *Flavobacterium*, and *Pseudomonas*) and one yeast (*Rhodotorula*) for comparison to municipal seed. A Warburg respirometer was utilized according to the Umbreit (1972) procedure. 2,4-DNT was rapidly degraded by industrial seed and even demonstrated stimulation above 200 mg/L. Municipal seed demonstrated inhibition at all concentrations. 4-methyl-3- nitroaniline was detected as a metabolite in the reactor containing the industrial seed. Similar results were obtained with 2,6-DNT, except 2-methyl-5-nitroaniline was formed as a by-product.[9] Another article presented thorough respirometer work on TNT wastewaters.[10]

Communications with researchers indicate that current biological efforts are successfully breaking the aromatic ring of 2,4-DNT.[2,3] Research is being performed on microorganisms which have been exposed to toxic compounds such as TNT and 2,4-DNT and determining if metabolism of the compounds occurs. Early results indicate that both compounds can be completely biodegraded.

Concerning the formation of toxic or mutagenic compounds during biotransformation of DNT, both oxidative and reductive metabolism from microorganisms contribute to the formation of mutagenic products from 2,4-DNT and its metabolites in vitro. The products studied were 2,4-DNT, 2,4-DAT, 2A4NT, 2,4-dinitrobenzoic acid, 2-amino-4- nitrobenzoic acid, 2NO4NT, and 2,4-dinitrobenzyl alcohol. In summary, 2,4-DNT and 2,4-DAT (the end product of the metabolism) were less mutagenic by ~8-80 times than the intermediate metabolites.[11] A review on TNT with references to DNT in the text, indicates that DNT has no effect on activated sludge.[12]

Activated Carbon Treatment

The adsorption of 2,4-DNT in aqueous solution by two commercial activated carbons was evaluated. Additionally, the desorption of DNT from these adsorbents by solvent extraction were studied. The efficiency of removal of DNT from aqueous solution by Calgon Filtrasorb® (FS)-300 and FS-400 are different, as FS-400 had the greatest capacity. FS-400 has a mean particle diameter of

1.0 mm while FS-300 has a mean particle diameter of 1.6 mm. Additionally, FS-400 has an iodine number of 975 min while FS-400 has 1,100 min. Grinding FS-300 increased its equilibrium adsorptive capacity, but not to the capacity of FS-400.[13]

Ho and Daw conducted carbon loading studies utilizing laboratory water containing 100 mg/L DNT and FS-400 carbon.[13] They determined that loadings of 800 mg of DNT per gram of FS-400 dry carbon were achieved. Additionally, some of the adsorbed DNT is converted to its derivatives. The presence of derivatives of 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, and 2,4-dinitrobenzoic acid indicates that one of the reactions is a side-chain (the methyl group) oxidation.[13]

In a second article GAC performance tests were conducted to evaluate treatment of pink water (munitions wastewater) from U.S. Army Ammunition Plants (AAPs). Comparative isotherm tests were conducted with five GACs to determine an optimum grade for pink water treatment and to evaluate temperature and compositional effects. The target effluent criteria of 0.04 mg/L for TNT, 0.03 mg/L for RDX or HMX, and 0.0007 mg/L 2,4-DNT were achieved with the isotherm tests.[14]

A third article involved treatment of wastewater containing five priority pollutants (7.9 mg DNT/L) in addition to fourteen other contaminants. Comparative assessments were performed for treatability by carbon adsorption, resin adsorption (XAD-4), and steam stripping (evaporation). Steam stripping was ineffective, while carbon adsorption was considered more cost effective than resin adsorption. Both adsorptive systems appeared to be capable of removing DNT to levels of 0.1 ppm or lower. Carbon was slightly more cost effective with a total annual cost of $2 to $3 per 1,000 L for flows of ~1,130 L/min and for removal down to 1 ppm.[15]

Analytical methodology involving GAC for extraction of 25 priority pollutants for analysis was also reviewed. Utilizing various displacers (methylene chloride, methanol and benz[alpha]anthracene-7,12-dione), the majority of the 25 pollutants were totally displaced. However, DNT was one of the pollutants which could not be totally displaced. The report recommended further work on DNT.[16]

An article dealing with TNT recommends the evaluation of water management and thermal regeneration of granular activated carbon. It recommended thermal regeneration since the treatment cost of 1,000 gal. of pink water could be approximately cut in half to a cost of $3.48/1,000 gal. of pink water treated.[17]

Incineration

Patent description of a process to first remove the water from the wastewater containing nitro compounds, and then incinerate, indicates that this method is five times more efficient than direct incineration.[18]

Oxidation

P. C. Ho of Oak Ridge National Laboratory (ORL) evaluated the synergistic effect of hydrogen peroxide (H_2O_2) and ultraviolet (UV) radiation from a medium-pressure lamp on the decomposition of 2,4-DNT in water was evaluated. The results indicated that the degradation pathways of DNT in aqueous solution are: (1) side-chain oxidation, which converts DNT to 1,3-dinitrobenzene, (2) hydroxylation of the benzene ring, (3) benzene ring cleavage, and (4) further photooxidation, which eventually converts the lower molecular weight acids and aldehydes to carbon dioxide (CO_2), water (H_2O), and nitric acid (HNO_3).[19]

The aqueous solutions were irradiated with either a 450-W (sometimes 200-W) Hanovia medium-pressure mercury vapor lamp (far-UV to infrared region) or a low-pressure mercury lamp (GE, G15T8), which has a maximum output at 253.7-nm. DNT in aqueous solution has an adsorption maximum at 252-nm. Additionally, H_2O_2 is photosensitive to UV light which was used to induce oxidation of compounds.[19]

The (ORL) experimental results indicated that the H_2O_2/DNT molar ratios for optimum degradation were determined to be 26 to 52. Both bulbs produced degradation; however, the presence of light in the far-UV region, as well as an excess of H_2O_2, was required for the degradation of DNT in aqueous solution.[19]

Intermediates identified in this study, after each photooxidation of aqueous DNT solution and of its degradation intermediates, suggest the following reaction pathway for photooxidation of aqueous DNT solutions with UV/H_2O_2:

2,4-DNT + H_2O_2 → UV 2,4-dinitrobenzyl alcohol → 2,4-dinitrobenzaldehyde → 2,4-dinitrobenzoic acid → 1,3-dinitrobenzene → 3-nitrophenol + dinitrophenols (+NO_3^-) → dihydroxynitrobenzenes → trihydeoxynitrobenzenes → nitromuconic acid derivatives (+NO_3^-) → maleic acid + nitro- and hydroxymaleic acid derivatives + glyoxal + glyoxylic acid (+NO_3^-) → oxalic acid + formic acid (+NO_3^-) → CO_2 + H_2O.[19]

Additional oxidation literature was reviewed which contained no references to DNT, but provided insight to potential treatment methodology. Wet air oxidation (WAO) for treatment of high COD (70,000 mg/L) wastewater was reviewed. WAO was recommended for wastes which are not biotreatable ($0.13/1,000 L), since WAO ($18/1,000 L) is an economically attractive method of treatment in reducing oxygen demand and altering the biotreatability versus hauling as a hazardous waste ($150-200/1,000 L plus shipping costs).[20] Several treatment methods were evaluated to treat wastewater from the production of utility poles, lumber, railroad ties, and other products treated with preservatives and fire retardant materials. Chemical coagulation/flocculation alone was eliminated due to an inconsistent ability to meet discharge standards. Biological methods were eliminated due to questionable performance with regard to pentachlorophenol removal, long lead time for procurement and construction, and the requirement for a constant rate of wastewater flow. Both activated carbon and UV/ozone were effective; however, the Ultrox International UV/ozone system was selected on the

basis of cost-effectiveness and the fact that the UV/ozone process destroyed the contaminants rather than transferring them to another medium.[21]

Ozone photochemistry and its degradative ability was evaluated. This effort demonstrated that the TNT aromatic ring was broken down to CO_2. No effort was performed on DNT.[22]

Advanced oxidation processes which utilized UV in conjunction with either ozone or H_2O_2 to generate hydroxyl radicals were reviewed. These radicals, in turn, attack and degrade organic molecules; no effort was performed on DNT.[23,24,25]

Reduction

Methods of electrochemical DNT reduction are contained in the literature; however, none proved to be economical. A nickel-based catalyst and various solvents were required for the reduction and several by-products were produced. The use of solvents to conduct the reactions makes this approach less economically attractive.[26]

Alkaline solutions of carbon monoxide in the form $Fe(CO)_5$ and water can be utilized to reduce DNT to 2,4-diaminotoluene.[27] The potential of analytical methodology utilizing silver electrodes to perform reduction was also investigated.[28] The reduction of DNT isomers produced during the manufacture of TNT with compounds such as ascorbic acid is possible.[29] Additionally, 2,4-DNT was reduced electrolytically to 2,4-DAT using titanic sulfate as the addition agent and no side products were obtained producing over 90% yields.[30]

General Wastewater Treatment

A form of powdered activated carbon treatment (PACT) process has been developed which lowers the organic concentration of the wastewater in conjunction with removing toxic compounds such as DNT. Chemical oxidants (permanganate, ozone and hydrogen peroxide) used for the destruction of organics such as DNT, may be extremely expensive as a treatment process due to the requirement of a large amount of oxidant. WAO is effective at degrading organics but requires an enclosed vessel, high temperatures, and pressures (typically 550°F and 2,000 psi).[31]

Direct filtration is often able to reduce toxics at the source by removal of suspended matter. (Generally all of the DNT is in solution in the wastewater; however, some form of filtration may be required to remove suspended matter to improve the treatment process.) Mono-media sand beds, microscreens, ultrafiltration units and membranes are several filtration devices. For gross-solids removal to a particle size of 1-5 micrometers, processes such as mono- or multi-media granular beds or microscreens are appropriate. A filtration method which borders on being a membrane process, ultrafiltration, is applicable for removing constituents of known molecular size, with the concentrated

sidestream being disposed of in another manner (e.g., incineration). Membrane systems are for concentrated, low-volume and relatively nonspecific waste streams and will retain all molecules falling within certain size ranges, depending on the membrane selected. The constituents on the permeate can be reduced by 50-99% and can be contained in 19-30% of the original volume. Again, the concentrate must be disposed of by other means such as thermal or chemical oxidation. "However, membrane concentration followed by thermal oxidation, although quite expensive as a wastewater treatment process, will be substantially less expensive than direct thermal oxidation of the entire waste stream."[31]

The removal of nitroaromatics from concentrated sulfuric acid can be accomplished using electrolysis; degradation proceeded to CO_2 and oxides of nitrogen.[32]

Membrane filtration has improved significantly due to its ability to survive harsh operating environments and reduce fouling by applying laminar flow through a tubular configuration. With a larger pore size, the resulting increased membrane flux greatly improves the operating economics.[33] While TNT successfully demonstrated the feasibility of membrane ultrafiltration in pink water; DNT demonstrated poor membrane rejection.[34]

"Washwater containing blasting oil from washing out residual nitric acid from the reaction mixture in a nitration plant is extracted with DNT, another common component of high explosives, in a mixer-settler apparatus." The DNT was extracted with toluene from the wastewater. Authors were concerned with DNT in the wastewater only because of the addition of nitrates.[35]

Another article concerning methodology for analysis of DNT indicated specified levels of sensitivity at 0.05 ppb for 2,4-DNT and 2,6-DNT, but cautioned that this may not be applicable to various forms of wastewater due to additional contamination.[36]

"Research is being conducted to investigate closure methods for lagoons containing TNT and RDX wastes (pink water). Research has included (1) an evaluation of existing asphalt encapsulation techniques for hazardous wastes, (2) an evaluation of alternative heating/mixing systems, (3) review of the properties of various asphalt products that may be used, (4) laboratory experiments of the temperature and holding times required for thermal breakdown of the various compounds present in the sludge, and (5) preliminary design of a pilot mixer/heating system." Heating experiments indicate a 90% reduction at a temperature of 250°C.[37]

"TNT was found to react in aqueous solution with surfactants containing amino and quaternary ammonium groups at pH 10-11 at ambient temperature. The surfactants investigated included N-tallow 1,3-diaminopropane, trimethyl N-tallow ammonium chloride and N,N, N',N',N'-Pentamethyl N-tallow 1,3-propane diammonium dichloride."[38]

"The major expense in this process for the treatment of Composition B wastewater is that of the surfactant, i.e., N,N,N',N',N'-pentamethyl N-tallow-1,3-propane diammonium dichloride, which is commercially available and is the surfactant of choice. Based on the assumption that the concentration of

the TNT in the water was 1 lb/1,000 gal. (120 mg/L) and required only 0.37 surfactant moles per mole of TNT, the cost of the surfactant would be $1.25 (April 1979) per 1,000 gal. of wastewater."[38]

TNT demonstrated the feasibility of surfactant technology utilizing Duoquad T-50; however, DNT required harsher treatment (55°C and pH-11.5) as poor or erratic removal was achieved at lower temperatures and lower pH.[39]

Health and Safety/Toxicity

From acute and chronic toxicity testing utilizing *Daphnia magna* and fathead minnows, 8.1 mg/L of DNT is recommended as the maximum allowable concentration and 0.12 mg/L recommended the maximum allowable 24-h average concentration by Environmental Protection Agency (EPA) methods.[40]

LABORATORY EVALUATIONS

Based on the literature reviewed, the following methods were recommended for laboratory evaluation for the following reasons: (1) various combinations of UV, ozone, and hydrogen peroxide treatment were recommended because of economics, ease of installation, and low operator involvement during operation; (2) development of biological degradation and/or accumulation should be monitored and various evaluations performed since recent information suggested successful breakage of the aromatic ring; and (3) adsorption isotherms should be developed with GAC and potential means for regeneration evaluated.

Biological Studies

The DNT biological studies were divided into three areas of investigation: toxicity, bioaccumulation, and biodegradation.

Toxicity Studies

The toxicity of a compound is generally assessed by measuring their repression of microbial respiration process. To assess the effect of these potentially toxic compounds; the microorganisms must be acclimated prior to the experiments, otherwise, repression of respiration will occur until the microorganisms acclimate themselves to the toxic compound.

The respirometer studies to evaluate the toxicity of DNT were performed with a Hach model 2173B BOD apparatus. The unit consisted of six individual reaction vessels that operated simultaneously during testing; each reaction vessel was connected to a separate manometer. The operation of the unit was based on oxygen utilization by the living microorganisms. As oxygen was used

in metabolism, CO_2 was produced as a by-product. In these units, the CO_2 gas chemically reacted with the lithium hydroxide which removed the CO_2 from the unit's atmosphere. The end result was a drop in pressure (measured by the manometer's) which was proportional to the rate of metabolism (BOD or oxygen utilization) of the microorganisms. All respirometer tests were conducted in a temperature range of 20 to 22°C.

The units operated in a range of 0 to 600 mg BOD/L. This was accomplished by using a total volume of seed and sample to be metabolized of 160 mL for each vessel. The seed was prepared using microorganisms removed from the BWTP RBC's. The 20 L container of seed (wastewater, contaminants, and microorganisms) was fed BWTP influent daily to maintain a representative acclimated biological culture for these studies. The quantity of seed necessary to provide sufficient quantities of microorganisms to inoculate the samples was determined to be 10 mL. The BOD of 100% seed was also measured for comparison; this was to assure that the seed strength was similar for all testing.

To assess toxicity, each evaluation compared seed strength (100%) and a blank (150 mL of sample without DNT plus 10 mL of seed) to the remaining units containing increasing concentrations of DNT in plant process water. A test matrix was developed utilizing solutions prepared in the range of 0 to 250 mg DNT/L with 100 mg/L of ethyl alcohol to provide an energy source for the microorganisms. If DNT proved to be toxic to the microorganisms, a reduction in respiration would occur with increasing concentrations of the DNT.

BOD results from the first series of tests did not indicate repression of microbial respiration. As can be observed in figure 10, no significant repression occurred at any of the DNT concentrations. A study of the chromatograms indicated that no DNT was detected in the solutions after 140 h of respiration (figs. 11 through 17). However, several by-products with various HPLC retention times (~2.93, 3.09, 3.53, and 5.08 min) were apparent in the solutions after the respirometer studies.

In the second test series (fig. 18), the microorganisms experienced repression in the initial period due to temperature shock from the use of reagents stored at 4°C to inhibit microbial growth prior to experimentation (procedure modified to prevent future problems). However, after a recovery period, vessels containing DNT responded similar to the blank. The 100% seed was not exposed to the effects of the temperature shock as can be observed in figure 18.

The third test series (fig. 19) indicated some form of repression occurred which temporarily repressed microbial respiration the first few days; the seed responded in a normal manner. Since the blank (0 mg DNT/L) also experienced initial repression similar to the DNT vessels, it would indicate that some unknown factor produced the repression and not DNT.

The fourth test series (fig. 20) indicated that the seed contained insufficient microorganisms. Following a lag period to allow multiplication of the microorganisms, normal respiration occurred. All DNT concentrations had a similar response, indicating no repression occurred.

In the fifth test series (fig. 21), no repression of microbial growth (BOD) was experienced. The seed responded in a normal manner. Figures 22 through 28 represent chromatograms from the individual respirometers from the fifth series of tests after ~170 h. The blank (fig. 22) which contains no DNT, shows no detectible compounds. The sample originally containing 50 mg DNT/L (fig. 23), had no DNT, but contained a peak at a HPLC retention time of 3.69 min. Figure 24, representing an initial concentration of 100 mg DNT/L, contained 21.1 mg DNT/L (retention time of ~6 min) and peaks at retention times of 1.72, 3.1, 3.64, and 7.17 min. Figure 25, representing an initial concentration of 150 mg DNT/L, contained 47.2 mg DNT/L and peaks at retention times of 1.79, 2.99, 3.53, and 7.02 min. Figure 26, representing an initial concentration of 200 mg DNT/L, contained 44.5 mg DNT/L and peaks at retention times of 1.77, 3.06, 3.59, and 7.13 min. Figure 27, representing an initial concentration of 250 mg DNT/L, contained 88.6 mg DNT/L and peaks at 1.76, 3.10, 3.64, and 7.14 min. Finally, figure 28 which represents 100% seed contained no DNT nor any other detectible compounds.

In conclusion, the DNT was not toxic to acclimated biomass. The DNT produced four by-products after 160 h of reaction. These by-products are represented by HPLC retention times of ~1.75, 3.05, 3.5, and 7.1 min when DNT has a retention time of 6.0 min. As demonstrated later by the biodegradation experiments (refer to the Biodegradation section), the compound with a retention time of 1.75 min is apparently a component of the biomass.

Bioaccumulation

Two biomass/bioreactors each containing 20 L of biomass (<1%) and BWTP influent wastewater were evaluated to assess the effects of bioaccumulation. The first reactor was utilized as a blank and the second reactor was operated essentially identical to the first reactor with the exception that DNT was supplemented to the feed (which occasionally resulted in leakage of DNT). Six L of the contents of each reactor were removed on a daily basis (except on weekends and on day 5) and replaced with fresh wastewater from the influent of the BWTP to provide a carbon source for the microorganisms. The DNT supplemented reactor also had an additional L removed and replaced with a more concentrated solution of DNT (58.6 mg DNT/L) in water. Samples were periodically collected and analyzed for the concentration of DNT and measurement of COD (table 9) to assess bioaccumulation and its effects.

Figure 29 represents a HPLC chromatogram of the blank biomass/bioreactor. The observed peaks represent background peaks which can be observed throughout the evaluation. Figure 30 represents a chromatogram of the DNT supplemented biomass/bioreactor prior to DNT addition. DNT can be observed indicating the presence of a small quantity of DNT in the wastewater feed (3.06 mg/L at a retention time of 4.61 min).

At the end of day one, figure 31 indicated no DNT nor any unusual peaks for the blank. However, figure 32 indicated the DNT supplemented biomass/bioreactor contained both DNT (retention time ~4.8 min.) and potential biodegradation by-products (peaks) with retention times of 3.53, 3.79, and 5.68

min. On day 4, the blank (fig. 33) was normal while the DNT supplemented reactor (fig. 34) demonstrated peaks at 2.72, 2.99, and 3.82 min and no DNT. On day 6, the blank was normal (fig. 35) while the DNT supplemented reactor (fig. 36) demonstrated peaks at 2.86, 3.11, 3.56, and 5.14 min and 0.07 mg DNT/L. On day 7, the blank was normal and contained 0.08 mg DNT/L (fig. 37) while the DNT supplemented reactor (fig. 38) demonstrated peaks at 2.54, 3.02, and 3.70 min and 1.24 mg DNT/L. Day 8 blank was normal with the exception of an unknown peak at 5.46 min (unknown compound in the influent to the BWTP) and a DNT concentration of 0.74 mg/L (fig. 39). The DNT supplemented reactor (fig. 40) demonstrated a peak at 2.48 min and contained 0.99 DNT mg/L. Day 11 was normal with the exception of an unknown peak at 2.96 min and a DNT concentration of 0.02 mg/L (fig. 41). The DNT supplemented reactor contained 10.62 mg DNT/L and no significant peaks (fig. 42). Day 12 blank was normal with the exception of an unknown peak at 5.42 min and a DNT concentration of 0.07 mg/L (fig. 43); the DNT supplemented reactor contained 0.02 mg DNT/L and had an unknown peak at 3.63 min (fig. 44). Days 13, 14, and 15 (fig. 45 through 50) indicated no DNT nor the presence of any unknown peaks.

This evaluation indicated that instead of bioaccumulation occurring, DNT was biodegraded and produced up to six unknown by-products with HPLC retention times of ~2.6, 2.9, 3.1, 3.5, 3.6, and 3.75 min (table 9). As time proceeded and permitted the microorganisms in the DNT supplemented reactor to become acclimated to the DNT and DNT by-products, the peaks for the by-products are no longer present indicating further biodegradation. Additionally, an unknown contaminant from the wastewater could be observed at an average HPLC retention time of 5.55 min. Unknown number 2 (2.9 min.) appeared at day 11 of the evaluation in the blank reactor due to the presence of DNT from the wastewater feed from the BWTP during the period of days 7 through 12. Otherwise the contaminants appeared only in the DNT supplemented reactor. An unknown contaminant from the BWTP was detected on days 8 and 12 in the blank and day 1 for the DNT supplemented reactor.

Additionally, several experiments were performed with the BWTP RBC biomass to ascertain if DNT accumulated in the biomass and if current analytical methods could detect the presence of DNT. Analysis of the RBC biomass showed only trace quantities of DNT by HPLC analysis. Digestion of the biomass with sulfuric acid for 30 min. did not demonstrate any greater quantities of DNT detected.

Biodegradation Studies

The Hach BOD apparatus was also used in studies ranging up to further define the biodegradability of DNT by performing three evaluations. Samples were removed from the vessels at different time intervals for HPLC analysis, to observe DNT degradation, and the formation and degradation of by-products. Additionally, the test matrix developed to assess the biodegradability of DNT held the concentration of DNT constant to operate all vessels identically for each series of tests (70.9 mg DNT/L for tests 1 and 2; 35.4 mg DNT/L for test 3). Sufficient alcohol was added to assure the presence of an energy source for the microorganisms in the range of 600 to 900 mg BOD/L.

Table 10 contains the results of the first biodegradation study. The table is divided into two sections to allow correlation of the data. The top half represents the progression of metabolism through measurement of BOD's by the manometers, while the bottom half corresponds to sampling of the reactors at various time intervals, and measurement of COD (indicative of quantity of remaining organic material) and DNT concentration.

Figures 51 through 57 are chromatograms of the samples as time progressed, while figures 58 through 64 are chromatograms of the final content of each reaction vessel at the end of the experiment. It should be noted that the removal of 10 mL of the contents of each vessel for sampling had a slight effect on the BOD's; however, it was not considered significant. Figure 51 represents the chromatogram of the seed which contained two small peaks (retention times of 1.64 and 1.94 min). These small peaks should not be observed during the experiment due to the dilution of the seed. However, the peaks reappeared as time progressed indicating that they were due to microbial growth. Figure 52 represents the chromatogram of the initial nutrient water which contained all components including 70.9 mg DNT/L at a retention time of 5.88 min; no other peaks were present. Figure 53 represents the chromatogram of vessel 1 at 23 h. In this case, 24.7 mg/L of DNT was present and six peaks were detected at retention times of 1.77, 1.95, 2.07, 3.86, 7.45, and 8.42 min. After 77 h, a sample taken from vessel 2 (fig. 54) contained no DNT and five peaks (retention times of 1.34, 1.87, 2.85, 3.75, and 4.03 min). At 95 h (fig. 55), vessel 3 contained no DNT and seven peaks (1.63, 1.84, 1.98, 2.45, 2.95, 3.80, and 4.02 min). At 119 h (fig. 56), vessel 4 contained no DNT and six peaks (1.74, 1.87, 2.00, 2.42, 3.82, and 4.04 min). At 144 h (fig. 57), vessel 5 contained no DNT and six peaks (1.34, 1.80, 1.84, 2.03, 2.41, and 3.78 min).

At 168 h the experiment was concluded and all reaction vessels examined for DNT, COD, and peak grouping analysis. Figure 58 represents a chromatogram of the blank and a peak present at a retention time of 1.72 min, thereby confirming that this peak was a component of the microorganisms. Smaller peaks were also observed at 1.96 and 2.03 min. Figure 59 represents vessel 1; no DNT was detected and seven peaks were present (1.69, 1.83, 1.97, 3.59, 3.80, 7.55, and 8.53 min). Figure 60 represents vessel 2; no DNT was detected and four peaks were present (1.67, 1.90, 1.97, and 3.83 min). Figure 61 represents vessel 3; no DNT was detected and three peaks were present (1.67, 1.82, and 1.96 min). Figure 62 represents vessel 4; no DNT was detected and five peaks were present (1.66, 1.82, 1.96, 2.45, and 3.80 min). Figure 63 represents vessel 5; no DNT was detected and five peaks were present (1.64, 1.83, 1.94, 2.42, and 3.76 min). Figure 64 represents vessel 6; no DNT was detected and five peaks were present (1.67, 1.81, 1.97, 2.40, and 2.69 min).

Table 11 contains a grouping of the various peaks identified from the biodegradation experiment. A total of 12 peaks were identified (DNT is the peak at 6.0 min). Peaks with retention times of 1.7 to ~2.0 min represent compounds related to the biomass contained in the reaction vessels. From 1.3 to 8.4, six to nine peaks were observed as by-products from the degradation of DNT. As time progresses the microorganisms acclimate and less by-products are observed.

Table 12 contains the results of the second biodegradation study. Figures 65 through 70 are chromatograms of the samples as time progressed, while

figures 71 through 78 are chromatograms of the final content of each vessel at the end of the experiment. No chromatogram of the seed was taken on this experiment; however, the previous biodegradation experiment indicated that peaks with retention times of ~1.7 and 2.0 min were attributed to the biomass. In this biodegradation study the peaks were again present throughout the chromatograms as time progressed further confirming that they were due to microbial growth. The initial nutrient water contained all components including 70.9 mg DNT/L. Figure 65 represents the chromatogram of vessel 1 at 22 h. In this case, 0.08 mg/L of DNT was present and three peaks were detected at retention times of 1.69, 1.81, and 2.03 min. Here, biodegradation occurred at a more rapid rate indicating that the microorganisms were more acclimated to the DNT. After 94 h, a sample taken from vessel 2 (fig. 66) contained no DNT and three peaks (retention times of 1.64, 1.80, and 2.01 min). At 118 h (fig. 67), vessel 3 contained no DNT and four peaks (1.68, 1.97, 2.51, and 2.69 min). At 142 h (fig. 68), vessel 4 contained no DNT and three peaks (1.68, 1.97, and 2.61 min). At 166 h (fig. 69), vessel 5 contained no DNT and three peaks (1.65, 1.81, and 1.95 min). At 190 h (fig. 70), vessel 6 contained no DNT and three peaks (1.72, 1.82, and 1.97 min).

At 264 h the second experiment was concluded and all reaction vessels were examined for DNT and peak grouping. Figure 71 represents a chromatogram of the nutrient water and has peaks at retention times of 1.64, 1.83, and 1.98 min indicating that these peaks were a component of the microorganisms. Additionally, there were two broad peaks at 2.96 and 3.18 min. Since no broad peaks of this nature had been observed previously in any samples, it was suspected that these peaks were contaminants from previous samples processed through the HPLC. Figures 72 through 78 represent vessels 1 through 7. No DNT was detected and only the biomass peaks were present.

Table 13 contains the results of the third biodegradation study which was performed at a lower DNT concentration (35.4 mg DNT/L). Figures 79 through 85 are chromatograms of the samples as time progressed, while figures 86 through 94 are chromatograms of the final content of each vessel at the end of the experiment. A chromatogram of the seed taken during this experiment indicated no DNT and two peaks with retention times of 1.46 and 1.83 min (similar to previous biodegradation experiments indicating that peaks with retention times of ~1.7 and 2.0 min were attributed to the biomass). In this biodegradation study, these peaks were again present throughout the chromatograms as time progressed, further confirming that they were due to microbial growth. The initial nutrient water (fig. 80) contained all components including 35.4 mg DNT/L. Figure 81 represents the chromatogram of vessel 1 at 24 h. In this case, no DNT was present and 1 peak was detected at a retention time of 3.62 min. After 48 h, a sample taken from vessel 2 (fig. 82) contained no DNT and four peaks (retention times of 1.67, 1.99, 3.82 and 4.03 min). At 170 h (fig. 83), vessel 4 contained no DNT and five peaks (1.63, 1.79, 1.8, 1.94, and 3.72 min). At 216 h (fig. 84), vessel 5 contained no DNT and four peaks (1.70, 1.84, 2.02 and 4.62 min). At 264 h (fig. 85), vessel 6 contained no DNT and seven peaks (1.04, 1.76, 1.99, 2.40, 2.69, 3.6, and 4.55 min).

At 337 h this experiment was concluded and all vessels examined for DNT and peak grouping analysis. Figure 86 represents a chromatogram of the seed and the presence of peaks at retention times 2.04 through 6.87. Figure 87

represents a chromatogram of the nutrient water and peaks present at retention times of 1.05, 1.70, 2.03, and 4.63 min. Figures 88 through 94 represent vessels 1 through 7. No DNT was detected and several biomass peaks were present. Additionally, a couple of unknown peaks appeared in some of the samples.

Experiment 1 identified a total of 12 peaks in addition to the DNT peak. Peaks with retention times of 1.7 to ~2.0 min were determined to represent compounds related to the biomass contained in the vessels. From 2.0 to 8.4 min, six to nine peaks were observed as by-products from the degradation of DNT. In experiments 2 and 3, biomass peaks were observed throughout the experiments but only a few biotransformation products were observed.

In summary, DNT was biotransformed into several unknown by-products which can be detected by HPLC. The retention times for the unknown peaks decrease as time progresses for the experiment indicating that the reactions may be proceeding to more polar and possibly more degraded molecules. Additionally, there were indications from these experiments that the microorganisms may have completely utilized the DNT.

UV, Ozone, H_2O_2, UV/H_2O_2, UV/Ozone

Information from the literature review indicated UV/H_2O_2 and UV/ozone treatment of DNT in wastewater yielded CO_2, H_2O and other basic molecules which indicated breakage of the aromatic ring of DNT. Therefore, to assess these various combinations, equipment to generate UV radiation and ozone gas was assembled and preliminary laboratory-scale evaluations were performed to determine the parameters to be evaluated during the bench-scale testing.

The 254-nm UV light source was a Mineralight Lamp model R-520 manufactured by UVP Inc. The light flux was quantified utilizing a Spectroline model DM-254N UV meter by Spectronics Corporation and was determined to average 5-mW/cm^2 during experimentation. The UV lamp was enclosed in a cardboard box to limit personnel exposure. The ozone was produced by an Airox Ozonator model C2P-3C-2 by Pollution Control Industries, Inc. The ozone was introduced using the delivery end of a disposable polyethylene pipette connected to the source and was not quantified. The stock H_2O_2 was 30% by weight and was diluted to ~1-3% upon mixing with solutions containing DNT. The UV experiments were conducted utilizing 1-cm pathlength quartz cells from various vendors. The ozone and H_2O_2 experiments were conducted in small quartz test tubes.

Table 8 contains the results of the experiments and represents DNT concentrations in relation to duration of exposure to the various treatment methods. UV, ozone, and H_2O_2 exposure was ineffective as can be observed from table 8. The combination UV/H_2O_2 resulted in a significant improvement in DNT degradation; however, UV/ozone resulted in nearly complete degradation after 5 min of exposure. Finally, UV/ozone was applied to actual water dry wastewater which resulted in degradation at a lower rate. This was expected since the wastewater contained additional components that would compete for the hydroxyl radicals.

The results (table 14) of the testing concluded that the combination of UV light and ozone destroyed the DNT and this approach should be further investigated in the bench-scale studies.

Granular Activated Carbon Isotherms

Adsorption isotherms were developed for removal of 2,4-DNT from WD wastewater, solvent-fortified WD wastewater, and BWTP effluent by FS-400 activated carbon.

Optimization of Adsorption Time

Before isotherms could be conducted, the time of contact between DNT and FS-400 had to be determined. Six samples of ~20 mg of FS-400 were weighed. To each sample 100 mL of a known DNT concentration was added. Each sample was shaken on an orbital shaker at 200 rpm. Samples were removed from the shaker at 1-h intervals for 2 h, and 30-min intervals afterwards, until a total time of 240 min had elapsed. Data, shown in table 14 and figure 95 indicate that 2 h of contact time, with shaking, sufficiently brings the solutions to equilibrium. However, since the adsorption appeared to be linear from 0 to 2 h, 1 h was chosen as the contact time for the isotherms' work which resulted in approximately 50% of the total adsorption.

Isotherms

Adsorption isotherms were determined by adding increasing amounts of FS-400 to a solution of WD wastewater. After the 1-h contact time, the liquid was removed from the bottle, filtered, and analyzed for DNT content by HPLC. A sample of the DNT solution that had not been in contact with FS-400 was analyzed to determine initial concentration. The amount of DNT adsorbed by each gram of FS-400 in the 1-h period was determined and plotted versus final DNT concentration on a log-log scale. The maximum carbon adsorptive capacity extrapolation of the regression line intersection with the initial concentration of the DNT solution) would be ~200 mg DNT per gram of FS-400 for 1-h contact time. The adsorption isotherms for this WD wastewater are presented in figure 96, and the raw data in table 16.

Additionally, an isotherm was established for the same WD wastewater with ~1.5% alcohol and 0.6% ether by weight. The addition of these solvents to the water was to provide indication of the competition for adsorptive sites of the three compounds. The experiment was conducted in the same manner as the previous work and indicated that the maximum carbon adsorptive capacity would be ~100 mg DNT per gram of FS-400 in 1 h. The data are presented in table 17 and the isotherm in figure 97. The reduction in ether concentration observed indicates that preferential adsorption of ether may be occurring.

Finally, the isotherm for a sample of BWTP effluent (collected on 9-11-90) with DNT added was determined. The DNT concentration was less than 2.0 mg DNT/L since the wastewater characterization section indicated that the plant effluent rarely exceeded this concentration. The data are presented in table 18 and the isotherm in figure 98. It is obvious that the maximum carbon adsorptive capacity is greatly decreased, and appears to reach a maximum of about 1.8 mg DNT/g FS-400 in the 1-h of contact time.

In summary, the maximum carbon adsorptive capacity of about 200 mg DNT/g FS-400 in 1-h contact time was seen in the WD wastewater with no additional solvents added. Since ~50% of adsorption occurred in 1 h, DNT loading was estimated at 400 mg DNT/gm of FS-400 carbon. This was reduced ~50% when exposed to high solvent concentrations. Additionally, the BWTP effluent showed a DNT adsorptive capacity, which was significantly reduced because other organics competed for adsorption sites.

BENCH-SCALE EVALUATIONS

A test plan was developed for the UV/ozone and GAC bench-scale evaluations (appendix A) to isolate and vary individual parameters to define optimum operating conditions. The biological evaluation was continued without a test plan since the principal objective was to develop microorganisms on an RBC which could utilize DNT and optimization was beyond the scope or funding of this effort.

Biological

A schematic of the bench-scale unit is presented in figure 99. The bench-scale RBC consists of nineteen 9-in. diameter by 1/4-in. thick discs mounted on a horizontal shaft which rotates through a 10-L liquid reservoir containing wastewater. Rotation is effected by a variable speed motor with controller. Approximately 40% of the disc surface, to which the biomass growth adheres, is submerged. As the contactor rotates through the wastewater reservoir, it is alternately contacted with air and the wastewater contained in the reservoir, resulting in the biological reduction. Four stages are separated by bulkheads, each of which has a 1-in. diameter hole located near the bottom to provide for continuous flow through the reservoir. Following the fourth stage a weir is provided for wastewater containment and effluent overflow from the final compartment for discharge.

Figure 100 is a photograph of the bench-scale RBC during operation. A closeup of the RBC biomass (microorganisms) is contained in figure 101. An effluent collector (fig. 102) was utilized to collect and observe what occurred to the microorganisms after exiting the RBC.

The RBC was evaluated for a period of 71 days. During this period a number of adjustments to microbial seed, RBC flow rate, and RBC DNT influent concentrations were made which assisted in achieving biodegradation of DNT.

Continuous influent flow consisted of three individual streams: (1) simulated wastewater, (2) phosphate feed, and (3) nitrate feed. The three streams utilized separate pumping systems to deliver an average composite influent during the biodegradation period (days 42 through 71) comprised of 400 ± 60 mg COD/L, 0.4 ± 0.3 mg phosphates/L as "P", and 29 ± 11 mg nitrates/L as "N". The total influent flow ranged from 35 to 70 mL/min. DNT was added at concentrations ranging from 15 to 55 mg DNT/L. The surface area of the RBC discs is 16.8 ft^2, which translates to a hydraulic loading of 1.58 gallons per day/ft^2 of surface area and an organic loading of 5.3 lb COD per day/1,000 ft^2 of surface area at a flow rate of 70 mL/min (approximately 2.4-H residence time). Rotational speed was maintained at 7 rpm which was previously determined to be the optimum speed to provide sufficient aeration and prevent excessive sloughing of the biomass from the disc surfaces.[41]

In order to initiate microbial growth on the disc surfaces, the system was seeded with biomass obtained from the biological wastewater treatment facility. The reservoir was filled to volume with simulated wastewater containing 100 mg ethanol/L (carbon source) and supporting nutrients (nitrates and phosphates). The unit was operated under a static hydraulic load for six weeks (i.e., no continuous influent feed) until a sufficient growth accumulated on the disc surfaces to support a continuous influent feed. The system was then converted to normal operation (i.e., continuous feed) on what was designated day 0. Sampling of influent and effluent streams was initiated and COD removal efficiency was monitored observing for stable conditions prior to the addition of DNT. The flow diagram of figure 99 contains the RBC sample locations. Sample locations B-1 and B-2 are where 20-mL samples were taken for COD, nitrates, phosphates, and DNT.

On days 20 through 71 the RBC microorganisms were exposed to DNT concentrations of ~18-65 mg DNT/L. Samples of the influent, effluent, and biomass were analyzed for DNT and DAT (potential end product of biotransformation reported in the literature). Previous DNT biological studies and characterization efforts (wastewater and biomass) performed for this project involved either dilute or extremely intermittent flows, which may have not allowed for complete acclimation of the biomass to the DNT. This investigative method attempted to achieve improved removal efficiency through greater control of DNT exposure with the RBC.

The COD removal efficiency of the RBC from the beginning to the end of the evaluation is shown in figure 103. Sampling was initiated after sufficient microbial mass had developed on the RBC. COD removal efficiency of greater than 90% is usually achievable once the biomass acclimates unless the RBC is disturbed or toxicity is experienced. As shown in figure 103, the COD removal efficiency increased from ~50% to greater than 90% prior to the addition of DNT at an influent flow rate of 70 mL/min. The addition of DNT, after 20 days, resulted in a significant decrease in removal efficiency; however, efficiency increased until the flow rate was reduced 50% (38 mL/min) at day 41. After day 50, the removal efficiency was greater than 90% until the end of the evaluation when a DNT-alcohol feed pump failure occurred over an estimated two-day period.

The DNT removal efficiency of the RBC is represented in figure 104. Initial sampling indicates that the DNT may have absorbed onto the RBC biomass

until a limit was reached and then absorption decreased (day 21). On day 29, the RBC was reseeded with fresh microbial mass from the wastewater treatment facility in an attempt to increase microbial degradation of DNT (since natural selection may have eliminated the DNT degrading microorganisms during the six-week development stage). DNT removal efficiency increased only slightly over the next 12 days; therefore, doubling the residence time by (decreasing the flow rate to 38 mL/min) was evaluated starting on day 41. Doubling the residence time of the RBC to allow a longer time period for biodegradation resulted in a significant increase in the removal efficiency of DNT from the simulated wastewater. DNT removal of 100% was achieved with ~26.5 mg DNT/L in the influent until the influent concentration increased (50%) to 39.2 mg DNT/L (day 48). The microorganisms were in the process of acclimating to the increase in DNT concentration when a four-hour power failure occurred (day 49) and allowed the system to become anaerobic. The effects of a system becoming anaerobic cannot be determined since the power failure occurred prior to a weekend when no sampling was performed. By day 53 the microorganism had recovered and 100% DNT removal was again achieved. On day 54 the flow rate was increased to 50 mL/min (66% of original) which resulted in a temporary decrease in removal efficiency for DNT. Examination of the HPLC chromatograms on day 57 revealed the presence of unknowns in the effluent. On day 62, the flow rate was increased to 75 mL/min and 100% DNT removal was briefly achieved prior to a major system failure which starved the microorganisms for several days. During days 67 through 71, the microorganisms attempted to recover while the concentration of influent DNT was increased from ~18.6 to 36.8 mg DNT/L.

Photographs of the biomass (microorganisms) during the process of acclimation were taken. Figures 105 and 106 are photographs of the biomass in each of the four stages of the RBC on day 26. Figures 107 and 108 are photographs of the biomass in each of the four stages of the RBC on day 35. Figure 109 has photographs of the biomass from a container placed at the effluent end of the RBC where DNT degradation was first confirmed. As can be observed, the biomass appears to become more fibrous as acclimation occurs.

From these experiments, RBC microorganisms with an influent concentration in the range of 15 to 65 mg DNT/L supplemented with an organic energy source (ethyl alcohol), nitrates, and phosphates; successfully biodegraded DNT but was unstable over time. During the process of acclimation, the biomass appeared to become more fibrous. However, with significant influent fluctuations (hydraulic flow and DNT concentration) in the process, the decomposition rates decrease as observed in both the bench-scale RBC and the plant scale RBC. This may indicate that the organisms require further control of biological conditions or that biotransformed products may be toxic to the biomass under certain conditions.

UV/Ozone

A Normag photoreactor was utilized for these bench studies to evaluate degradation of DNT (fig. 110). The Normag photoreactor was selected as the most compatible equipment due to the ability to add ozone, provide constant agitation, control temperature, and irradiate the sample with different types of UV radiation while withdrawing samples as the reaction proceeded.

The dimensions of the reactor were: 700-mm height, 260-mm width, and 100-mm depth. The 350-400 mL capacity reactor uses forced liquid circulation with a glass pump and Hostaflon-coated pump rotor. The reactor required modification to improve circulation and sampling which resulted in a larger reactor volume as will be detailed later. The gas exiting the unit was bubbled into water to reduce any emission of ozone into the laboratory. The jacketed reaction vessel permitted cooling of the solution being treated.

Two types of UV radiation sources were utilized with the Normag photoreactor. The mercury low-pressure lamp was used to produce intense radiation at the 254-nm mercury-resonance line. The mercury high-pressure lamp emitted in the short-wave UV region from about 240-nm to well into the visible range; the strongest line was 366-nm.

The ozone was produced using oxygen flowing through an Airox Ozonator model C2P-3C-2 (Pollution Control Industries Inc). The ozonator was designed to deliver ~1.5 to 0.6% ozone by weight at respective flow rates of 5 to 15 SCFH (higher flow rates diluted the ozone); however, laboratory analysis indicated ozone concentrations of 0.47, 0.30, and 0.23% at respective flow rates of 5, 10, and 15 SCFH.

Figure 111 contains a photograph of the assembled bench-scale UV/ozone reactor. Figure 112 contains (from left to right) the ozonator, the high pressure mercury bulb power supply, and the low pressure mercury bulb power supply. Figure 113 contains (from left to right) the high pressure mercury bulb, the low pressure mercury bulb, and the cooling jacket for the UV bulbs.

Synthetic wastewater was evaluated initially to separate and quantify the effects of several parameters which would be difficult to quantify in actual wastewater (table 19 and Appendix A). Tests 1 through 12 varied only the addition of ozone. This was to evaluate the effect of different flows of ozone which could assist in designing treatment facilities that maximize ozone addition since some locations may contain low quantities of organics. Tests 13 through 15 were designed to evaluate the effects of the high pressure lamp to compare its effectiveness in relation to the low pressure lamp. Tests 16 through 27 were designed to evaluate the effects of solvents on UV utilization and ozone consumption. Tests 28 through 30 and five additional tests were performed to determine design requirements for treatment facilities and to provide data for economic analysis based on actual wastewater.

Synthetic wastewater was prepared by mixing 100 mg DNT/L in distilled water. During initial testing and modification, the Normag photoreactor was determined to have a 410-mL capacity for the reactor. The selected UV bulb (two options) were inserted and the ozone generator (three flow rates) precalibrated prior to operation. The glass pump with the Hostaflon-coated rotor was started in addition to a second recycle support circulating pump (installed during debugging). Both the photoreactor and the ozone generator were started at time 0; collection times were varied in an attempt to minimize the loss of reactor volume. Upon completion of testing on synthetic wastewater, testing was performed on actual WD wastewater utilizing optimum conditions.

Figure 114 contains a flow diagram of the UV/ozone reactor and the sample locations. Sample location UV-1 is where ~2-mL samples were taken at various time intervals of 0 (blank), 1, 5, and 10.0 min during Test Plan tests 1 through 27 (synthetic wastewater). The time intervals varied during wastewater testing to determine the quantity of UV/ozone required for complete destruction of DNT. Sample location UV-2 is where ozone flow rates were monitored and concentrations determined.

The HPLC method was used for the detection of DNT and potential by-products (Appendix B). Wastewater samples were diluted 50/50 with methanol to dissolve any particulate DNT and filtered to remove any additional suspended matter and stored at room temperature for no more than 3 h. A series of ten standards from 0 to 200 mg DNT/L were prepared for calibration of the HPLC. After calibration, samples were analyzed with a final calibration check.

Several of the problems encountered with the Normag photoreactor during debugging were corrected by: (1) constructing a second pump recycle loop to improve reactor circulation, (2) performing adjustments to the air driven magnetic drive agitator to compensate for pressure drops that occurred at building 4703, (3) reducing sample volume (2-3 mL) and flushing prior to sampling (2-3 mL) by collecting samples off the second pump recycle loop, (4) reducing the number of samples taken to minimize the loss of reactor liquid, and (5) modifying the off-gas port to eliminate the loss of ~40% of reactor liquid during the bubbling that occurred during ozonation.

Synthetic wastewater experiments (Test Plan tests 1 through 27) were performed with the exception of tests 16 through 18 (table 19). These tests (16 through 18) were eliminated since prior tests indicated that ozone was required for DNT degradation. Five additional experiments were performed on the wastewater prior to tests 28 through 30 in order to develop optimum operating conditions. Finally, tests 28 through 30 evaluated different wastewaters at these optimum conditions.

Tests 1 through 12 (fig. 115) evaluated the quantity of ozone fed to the reactor by varying the flow rate of ozone. [Notes: (1) all UV/ozone data is contained in Appendix C, (2) the first min of each evaluation was excluded from calculations to provide time for ozone to reach the reactor and the output of the UV bulb to stabilize, and (3) the 100 mg DNT/L initial samples were near saturation concentration which resulted in a variance for HPLC analysis.] No significant difference in degradation can be observed during the 10-min reaction period other than ozone being required for the reaction to proceed. Comparison of tests 7 through 9 and 13 through 15 (fig. 116) indicates that 254-nm radiation is more effective since ozone flow was maintained at 10 SCFH while the high and low pressure bulbs were compared. Tests 4 through 6 and 19 through 21 compared the effect of the addition of ~4% solvents (2% ether, 2% alcohol) on degradation efficiency. The differences in these tests (fig. 117) do not appear to be significant at an ozone flow of 5 SCFH. Cursory measurement of COD during experimentation indicated that rapid stripping of the solvents occurs due to gas flow from ozonation. Figures 104 (comparison of tests 7 through 9 to 22 through 24) and 105 (comparison of tests 10 through 12 to 25 through 27) also compared the effect of the addition of 4% solvents at flow rates of 10 and 15 SCFH. In figure 118, DNT appears to be removed at a higher rate with the addition of

solvents. However, technical difficulties invalidated the results of the addition of solvents at 15 SCFH.

A sample containing 25 mg DNT/L was treated with UV radiation and a flow rate of 5 SCFH for ozone addition (fig. 119) for 10 min prior to the wastewater experiments to estimate the rate of DNT removal in the reactor. The removal of 5.46 mg DNT was accomplished from 1 to 10 min (0.61 mg DNT/min). This number was utilized to estimate the time required for complete degradation of DNT in wastewater.

Wastewater experiments were performed over extended periods of time to achieve a better understanding of the quantity of radiation and ozone required to achieve complete degradation of the DNT. The first wastewater experiment was for 120 min (fig. 120) which resulted in a reduction from 106.3 mg DNT/L to none detected during the period 5 to 120 min (destruction rate of 0.92 mg DNT/min). Figure 121, contains the results of varying the flow rate of ozone to the reactor. As reported previously, no significant difference was observed (-0.8 mg DNT/min was destroyed for all ozone flows rates).

Since the molar concentration of ozone for the various flow rates was similar due to dilution of the ozone at the higher flow rates, the most economical condition 5 SCFH was chosen for the final tests (tests 28 through 30). The wastewater for the first test was a mixture of LKL (primary) and M6 formulations. The wastewater for the second test was a mixture of M6 (primary) and LKL propellant formulations. The differences of DNT concentrations for these wastewaters are shown in Appendix C. The third came from the effluent of the BWTP and even though the experiment resulted in complete removal of DNT, the results cannot be quantified due to the effects of high solids in the effluent wastewater interfering with reactor circulation. Figure 122 contains the results of the first two tests. Over the extended period of time, all of the DNT was removed at an average rate of 0.56 mg DNT/min. It should be noted that the efficiency of DNT removal decreases as the concentration of DNT decreases in the liquid.

Since the curve represented in figure 122 is approximately exponential, a first order plot of the data from the wastewater experiments during the period 5 to 245 min is represented in figure 123. Therefore:

$$\frac{dC}{dt} = -K_{obs}C$$

and

$$\ln(C/C_o) = -K_{obs}t$$

Where C and C_o are the instantaneous and initial concentrations of DNT and K_{obs} is the observed first-order rate constant.

Linear estimation of the line indicated a rate constant (slope) of -0.0161/min and a y-intercept of 0.19 with a correlation coefficient of 0.98.

Figures 124 through 129 represent the HPLC chromatograms for test 29 of the Test Plan. In figure 124, prior to the addition of UV/ozone, DNT is observed with a retention time of 5.73 min. After 5 min of exposure (fig. 125), by-products are observed at retention times of 1.41, 3.35, and 3.71 min in addition to the DNT peak. At 65 min of exposure (fig. 126), the same peaks are observed in different proportions. A new peak appears at a retention time of 4.34 min at 125 min of exposure (fig. 127). At 185 min of exposure (fig. 128), new peaks appear at 1.91 and 4.21 min retention times. After 245 min of exposure (fig. 129), the DNT and essentially all of the peaks have been eliminated.

By combining a Normag photoreactor and an Airox Ozonator in conjunction with several modifications, degradation of DNT and several unidentified by-products was achieved. It was determined that both UV radiation (254-nm) and ozone (5 SCFH) provided optimum conditions required for the reaction to proceed. Though the ozonator did not generate the prescribed concentration of ozone, data was generated that can be utilized for economic analysis. The results indicate that the DNT destruction rate is directly proportional to the quantity of UV radiation received by the sample. Additionally, since molar concentrations of ozone delivery was similar for all flow rates evaluated, further increases in the ozone flow rate was ineffectual in increasing the decomposition rate.

GAC Column Study

A single column length of 20 in. was utilized for the establishment of adsorption characteristics of actual wastewater. Figure 130 contains a photograph of the bench-scale GAC column and its support equipment. A 1-in. diameter Pyrex®-type glass GAC column was utilized with a measured void volume of 228 cc. A peristaltic pump was utilized for transfer of the influent to the column. The influent was stored in a 55-L tank while the effluent was collected by a fraction collector. The fraction collector consisted of 28 500-mL bottles. Connections between the components were made with Tygon® tubing.

Figure 131 contains a flow diagram of the GAC column and the effluent sample location (C-1). A daily sample was collected of the effluent along with a sample of the influent tank to quantify DNT adsorption. Additionally, flow rate and time were recorded. At sample location C-1, fractions of effluent were collected by the fraction collector until DNT was detected above the 0.5 mg/L threshold. This was accomplished by allowing the sample collector to collect effluent for one to three days and utilize up to all of the 28 500-mL bottles while processing the wastewater through the column. These bottles were labelled and the last bottle sampled and analyzed. If no DNT was detected, no further analysis was performed. When DNT was detected at breakthrough, all the bottles were analyzed until at least two adjacent bottles contained no DNT.

FS-400 GAC from the Calgon Carbon Corporation was utilized for the adsorption studies. The FS-400 has a density of 2.3 g/cc and a packing density

of 0.4 to 0.7 g/cc. Measurement indicated that the carbon had a void volume of 69.7%. The actual weight of the carbon in the column was determined to be 108.4 g carbon per 20 in. of height in the 1-in. column. Actual WD wastewater was utilized for the GAC column studies which contained DNT, ether, alcohol, and traces of DPA.

The proposed operating conditions (flow rate, total volume, and direction of flow) for the GAC tests are presented in table 20 from the Test Plan. Originally, six GAC column tests were proposed; however, only one test was completed due to the extensive time required to operate the column with actual wastewater. The GAC was backwashed with twice the bed volume of distilled water (~24 h) prior to testing to remove all fine particulate, air pockets, and stratify the carbon bed. After backwashing the GAC, actual WD wastewater was utilized to saturate the GAC. The reservoir was filled with the wastewater and continually replenished during the evaluation. The initial flow rate for the GAC studies was 3 mL/min; however, this flow rate was later increased to as great as 16 mL/min so that the minimum of four bed volumes/h could be processed. The influent pump was adjusted to control the flow to the column and a needle valve at the base of the column was adjusted to control the elution flow rate of the column. Finally, the fraction collector was operated to collect 500-mL samples until completion of the evaluation. Column loading was accomplished via downflow.

Additional testing was performed to determine if the solvents normally present in the wastewater streams could remove DNT from GAC or affect its adsorption capacity for DNT during intermittent high concentrations. To evaluate whether the solvents could desorb DNT, ~4.0% solvents by wt (estimated maximum that the carbon would be exposed to) were processed through the column after DNT breakthrough.

The analytical method that was used for the detection of DNT and potential by-products (Appendix B) utilized HPLC as previously detailed for the UV/ozone section. This same criteria was followed with the exception that the 3-h holding time for samples had to be extended to roughly 8 h to permit the laboratory time to process the quantity of samples generated.

During the GAC bench-scale evaluation, breakthrough occurred after 70 days. Table 21 contains daily influent and effluent sample analysis prior to breakthrough of the DNT through the column. The total volume processed was 330.5 L. The influent contained an average of 197.8 mg DNT/L. This resulted in a DNT loading of 65.4 g on 108.4 g of carbon, or 60.3 g DNT/100 g activated carbon. The influent concentration of ether was 68.0 $\pm$ 81.7 mg/L, while the effluent was 26.6 $\pm$ 38.1 mg/L. The influent concentration of alcohol was 584.5 $\pm$ 925.2 mg/L, while the effluent was 699.0 $\pm$ 910 mg/L. Traces of DPA were occasionally noted in both the influent and effluent. No DBP was observed in either the influent or effluent.

Table 22 contains the breakthrough data of DNT from the column. The 500-mL, first bottle after breakthrough, contained 3.4 mg DNT/L, no ether, and 240 mg alcohol/L. Approximately 22.35 L of influent were processed which contained an average of 278.6 mg DNT/L 300 mg alcohol/L, and 250 mg ether/L.

DNT concentration increased to 17.8 mg DNT/L while the effluent concentration of alcohol and ether were 250.4 ± 61.5 mg/L and 30.6 ± 37.5 mg/L, respectively.

After DNT breakthrough (day 71), solvents were added to assess the effect of desorption. Approximately 10.55 L of influent was processed which contained an average of 236.4 mg DNT/L, 13,125 mg alcohol/L, and 2,165 mg ether/L. DNT effluent concentration immediately increased to 25.9 mg DNT/L with the first bottle, fluctuated, and increased to 39.8 by the end of the period. The effluent concentration of alcohol and ether were 15,090.4 ± 724.0 mg/L and 1,056.4 ± 691.0 mg/L, respectively.

On day 73, the solvent concentration was decreased. Approximately 16.33 L of influent were processed which contained an average of 235.9 mg DNT/L, 6,520 mg alcohol/L, and 42.5 mg ether/L. DNT effluent concentration momentarily dropped to 35.4 mg DNT/L with the first bottle, and increased to a peak of 140.4 mg DNT/L and ended with a concentration of 113.4 mg DNT/L by the last bottle confirming the desorption effects observed with the isotherms. The effluent concentration of alcohol and ether were 6,496.1 ± 751.3 mg/L and 328.4 ± 300.2 mg/L, respectively.

Therefore, the column study utilizing actual wastewater achieved 60.3 mg DNT/100 mg carbon compared to 80% reported in the literature for pure water. Additionally, the effects reported from the isotherms for solvents were also observed.

ECONOMICS

Application of the particular treatment methodology for DNT wastewater abatement could be performed at three locations: (1) at the sites where the wastewater is generated (SR, WD, wet screening, and coating), (2) at collection points prior to the BWTP (MH 32 and 36), or (3) after the BWTP. Treatment at the sites would involve installation and maintenance of numerous facilities which would therefore be expensive to both install and operate. Treatment at collection points would reduce the quantity of wastewater for treatment, require at most only two treatment plants, and provide equalization of flow and concentration of contaminants. Treatment after the BWTP poses several difficult problems. First, the quantity of wastewater for treatment is ~5 times greater than the quantity at MH 32 where 90% of the DNT wastewater is generated. Secondly, the residual biomass and COD present in the BWTP effluent interferes considerably with the treatment process. Adsorption isotherms indicated that the competition for sites on the carbon did not permit the DNT to be fully removed after 1 h (0.5 mg/L remained), nor did it permit high removal (~2 mg/g carbon). With UV/ozone, settling for 30 min did not reduce the remaining quantities of biomass and COD to permit proper circulation in the reactor which prevented determination of the quantity of UV energy and ozone required for degradation (however, complete degradation was achieved).

An economic evaluation was performed utilizing collection of wastewater at MH 32. A rough order of magnitude (ROM) operating cost was performed for the technologies evaluated on the bench-scale level. As previously reported in the

Wastewater Characterization section, this location currently averages 180,000 gal./day of wastewater containing 9.8 kg DNT/day. The following data can be scaled-up to handle mobilization requirements.

Biological

The bench-scale RBC utilized wastewater which contained alcohol (energy source), phosphates, nitrates, and DNT. Implementation at MH 32 would involve possibly the addition of nitrates and phosphates and the energy source would be at least partially provided by the ether and alcohol in the wastewater (these parameters would have to be further defined). Biological treatment generally costs $0.13/1,000 L or $0.49/1,000 gal.[20] Utilizing these numbers, the daily biological treatment cost would be $88.57 (the treatment costs were not calculated from the limited bench-scale evaluation since the reference provided known treatment costs for full-scale biological wastewater treatment facilities).

UV/Ozone

The Normag photoreactor utilized a 15-W bulb to generate 1.82-W (measured) of 254-nm radiation (output efficiency = 12.13%) after passing through the cooling jacket. The estimated quantity of radiation that the liquid in the reactor received after compensating for the portion of output not utilized was 1.19-W (received efficiency = 7.93%). Degradation of 137 mg DNT occurred in ~0.4 L of wastewater over a period of 240 min. The current estimated cost of electricity at RAAP is $.035/kWh. These figures result in an estimated cost of $372.40/day for electricity or $2.07/1,000 gal. of wastewater. If the 7.9% UV output is adjusted to 20% for typical low pressure mercury bulbs, the costs are $149/day or $0.83/1,000 gal. of wastewater. It was calculated that 3.76 g of ozone was required during the 240 min of UV exposure to treat a DNT concentration of 137.4 mg DNT/L. Treatment of 9.8 kg of DNT would require 267.5 kg ozone/day or 588.6 lb/day.[42] If 7 kWh of electricity is required to produce a lb of ozone, this results in a cost of $144/day or $0.80/1,000 gal of wastewater. Therefore, the combined UV/ozone cost for treatment of DNT wastewaters at MH 32 is $293/day.

GAC

Since the adsorption results differed for the isotherms [0.4 gm DNT/gm carbon and 0.2 gm DNT/gm carbon when a high concentration of solvent (COD) was present] and the column study (0.6 g DNT/g carbon), 0.3 g DNT/g of FS 400 carbon was arbitrarily utilized for the economic analysis to conservatively represent any losses in efficiency during production operations. This would utilize the higher adsorption observed by the column (~60%) and the 50% reduction of adsorption due to solubilization of DNT by the solvents observed by the

isotherms. The cost of FS 400 in the range of 10,000 to 30,000 lb is $1.28/lb. Wastewater containing 9.8 kg of DNT would require 71.9 lb of carbon at this rate, or $92.03/day. Assuming that the carbon can be recycled, this estimated cost is $0.60/lb (based on previous regeneration of GAC for red water and consultation with the vendor) or and additional $43.14/day. Unfortunately, no estimate can be made on the operating cost of processing the carbon. Ignoring the operating cost, it is estimated that the cost of carbon is $135.17/day or $0.75/1000 gal.

HAZARDS ASSESSMENT

A preliminary hazards assessment was performed on UV/ozone and GAC for this project and a report was prepared by the RAAP Hazards Analysis department (Appendix D). Safety precautions were identified and recommendations are presented and discussed in the report.

CONCLUSIONS

1. New Federal and State regulations will necessitate the implementation of dinitrotoluene (DNT) abatement.

2. Four formulations of single-base propellant contain DNT and one formulation requires coating with DNT.

3. The water dry (WD) contributes 75% of the DNT; while wet screening (WS) and solvent recovery (SR) contribute 18 and 7%, respectively.

4. The biological wastewater treatment plant is estimated to degrade 98% of the DNT, but excursion periodically occurs.

5. Manhole (MH) 32 provides a cost effective treatment site to intercept and treat ~90% of the DNT-containing wastewaters (WD and WS). If the BWTP fails to treat the remaining quantity, MH 36 may be connected to a DNT wastewater treatment facility at MH 32.

6. Little or no DNT bioaccumulation was observed during biological experiments.

7. DNT did not demonstrate toxicity to acclimated biomass.

8. The DNT was subsequently biodegraded with ~6-9 by-products being observed by high performance liquid chromatography (HPLC) analysis. The identity and concentration of each by-product were not determined since these materials were further decomposed.

9. No 2,4-diaminotoluene (the reported end product of biodegradation of DNT) was detected during the biological experiments.

10. Though still not fully developed biological degradation achieved 100% degradation with a residence time of 2.4 h.

11. The biodestruction of DNT is not fully understood. Stability and by-product toxic effects, if present, require further investigation.

12. UV/ozone and GAC were effective in DNT abatement.

13. The cost of UV/ozone may have been negatively impacted due to the ozonator not operating as designed.

14. The study indicates that granular activated carbon (GAC) adsorption is a very effective method for DNT abatement. However, the carbon must subsequently be regenerated which adds to the treatment cost and safety concerns.

RECOMMENDATIONS

1. Utilize GAC as a short-term approach to meeting regulatory requirements since this technology is developed, reliable, and essentially available off-the-shelf.

2. Perform pilot-scale studies on UV/ozonation to further establish optimum operating parameters and assess economics.

3. Perform further research on biological degradation of DNT to further develop technology and reduce risks of implementation.

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LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

Term	Definition
DNT	2,4-dinitrotoluene
WD	Water dry
SR	Solvent recovery
WS	Wet screening
CO	Coating operation
RBC	Rotating biological contactor
	Biological treatment plant
UV	Ultraviolet radiation
	Ozone
H_2O_2	Hydrogen peroxide
GAC	Granular activated carbon
	Biological degradation
RAAP	Radford Army Ammunition Plant
AD	Air dry
Ether	Ethyl ether
Alcohol	Ethyl alcohol
COD	Chemical oxygen demand
DPA	Diphenylamine
DBP	Dibutylphthalate
NnDPA	N-nitroso-diphenylamine
HPLC	High performance liquid chromatograph
BOD_5	Five-day biological oxygen demand
TSS	Total suspended solids
SO_4	Sulfates
N	Nitrogen
MH	Manhole
4A	4-amino-2,6-dinitrotoluene
2,4DA	2,4-diamino-6-nitrotoluene
4,4'Az	2,2',6,6'-tetranitro-4,4'-azoxytoluene
4HA	4-hydroxylamino-2,6-dinitrotoluene
2A	2-amino-4,6-dinitrotoluene
2,2'Az	4,4',6,6'-tetranitro-2,2'-azoxytoluene
TAT	2,4,6-triaminotoluene
2,6DAT	2,6-diaminotoluene
2A4NT	2-amino-4-nitrotoluene
4A2NT	4-amino-2-nitrotoluene
2NO4NT	2-nitroso-4-nitrotoluene
4NO2NT	4-nitroso-2-nitrotoluene
	2,2'-dinitro-4,4'-azoxytoluene
	4,4'-dinitro-2,2'-azoxytoluene
	4-acetamido-2-nitrotoluene
	4-methyl-3-nitroaniline
	2-methyl-5-nitroaniline
	2,4-dinitrobenzoic acid
	2-amino-4-nitrobenzoic acid
	2,4-dinitrobenzyl alconol

Term	Definition
	2,4-dinitrobenzaldehyde
	Benz (a) anthracene-7,12-dione
	1,3-dinitrobenzene
	hydroxynitrobenzene derivatives
CO_2	Carbon dioxide
H_2O	Water
HNO_3	Nitric acid
PACT	Powdered activated carbon treatment
WAO	Wet air oxidation
TNT	Trinitrotoluene
nm	Nanometer
FS	Filtrasorb
ROM	Rough order of magnitude

Table 1. Water dry wastewater characterization data

	2,4-DNT concentration, mg/L			COD, mg/L O_2			Number tanks drained	
WD Tanks	1	2	3	1	2	3	WD	SR
Date								
10-17-89							2	0
10-18-89							2	8
10-19-89	161	154		3800	4325		2	17
10-20-89	251	271	213	2900	2425	4525	3	14
10-21-89	66	---		1000	---		2	5
10-22-89	75	---		1250	---		2	15
10-23-89	122	166		825	136		2	15
10-24-89	79	---*		34	8625*		2	4
10-25-89	404*	161*		8125*	1425*		1	0

Average (M1MP M67) 156 mg/L 2,4-DNT 2100 mg/L O_2
Average (M1MP M724) 282.5 mg/L 2,4-DNT 6100 mg/L O_2

*M1MP M724 propellant.

Table 2. Additional water dry wastewater characterization data

Description of source								
Propellant	M14	M6	M6	M6	M6	M6	M6	M6
Location (building)	WD	WD	WD	WD	WD	WD	WD	WD
Sample location	top tank	top tank	top tank	top tank	discharge line	discharge line	top tank	top tank
Date	4-30-90	4-30-89	6-15-89	6-21-90	7-18-90	8-14-90	7-30-90	8-22-90
Components (mg/L)								
DNT	262.9	241.3	150.2	259.3	360	370.0	326	335.5
COD	4950	6163	---	---	---	---	---	---
Ether	470	500	ND[1]	110	ND	290	390	290
Alcohol	380	240	trace	trace	ND	70	870	510
Acetone	---	---	---	---	---	---	---	---
DPA	---	---	---	---	2.57	3.84	---	4.74
DBP	---	---	---	---	---	ND	---	ND
NnDPA	---	---	---	---	---	ND	---	---
OD	---	---	---	---	---	---	---	---

[1] Questionable results since odor of solvents was present.

Table 2. (cont)

Description of source				
Propellant	LKL-120	LKL-120	LKL-120	LKL-120
Location (building)	WD	WD	WD	WD
Sample location	top tank	top tank	top tank	top tank
Date	6-28-90	7-26-90	8-10-90	8-16-90
Components (mg/L)				
DNT	127.0	31.8	47.4	55.3
COD	---	---	---	---
Ether	830	ND	ND	ND
Alcohol	9310	300	260	60
Acetone	---		---	---
2N-DPA	8.77	1.58	2.25	2.73
DBP	ND	ND	ND	ND
NnDPA	---	ND	---	---
OD	---		---	---
K_2SO_4	44.4		---	---

Table 3. Characterization of additional DNT wastewater sources

Description of source							
Propellant	M1MP M724	unknown	IMR	IMR	IMR	M1MP M724	M6
Location (building)	WS	WS	CO	CO	CO	SR	SR
Sample location	effluent	effluent	main basin	main basin	wash water	cool down wash water	cool down wash water
Date	10-25-90	---	5-30-90	5-31-90	5-31-90	10-25-89	8-16-90
Components (mg/L)							
DNT	10	13.2	110	78.9	ND	3	62.8
COD	20	56	256	187	3	825	---
Ether	---	---	1	ND	ND	---	960
Alcohol	---	---	10	11	ND	---	570
Acetone	---	---	---	0.7	ND	---	ND
2-NDPA	---	---	---	---	---	---	2.20
DBP	---	---	---	---	---	---	ND
NnDPA	---	---	---	---	---	---	ND
OD	---	---	---	---	---	---	0.404
K_2SO_4	---	---	---	---	---	---	

Table 4. Characterization of wastewater collection system and BWTP

	MH 32 (WD line)		MH 34 (40% of flow from Green Lines)		MH 36A (from SR Line)		MH 36B (combined flows)	BWTP	
Flow (MGD)									
Min-max	0.12-0.23		0.4-0.53		0.23-0.37			0.95-1.37	
Avg	~0.18		0.476		0.3			1.2	
COD (lb/day)									
Min-max	0-100		200-1000					300-9500	
Avg	~400		~500		~100			~4000	
Components	Composite	Grab	Composite	Grab	Composite	Grab	Grab	Grab	Grab
DNT	6.4	75.82	0.47	ND	0.54	ND	ND	4.27	ND
Ethanol	---	495	---	180	0.20	3.4	215	40	1.3
Ether	---	9.3	---	1.6	2	1.3	1.9	4.9	ND
Acetone	---	ND	---	ND	---	ND	ND	ND	ND
NG	---	ND	---	ND	---	ND	ND	---	---

[1] Composite - 24-h composite of concentration.
[2] Grab - One-time grab samples for comparison.

Table 5. Relationship of DNT release to the wastewater collection system with respect to one WD tank (40,000 lb)

Process location and source	No. required	Quantity of wastewater	DNT conc (mg/L)	DNT load (kg)	Total DNT load (kg)	Fraction of total contribution (%)
SR	2 buildings					
Process water		1,250 gal./bldg	62.8	0.6	0.8	7
Motive water		3,790 gal./bldg	6.4	0.2		
WD	1 tank					
Process water		7,000 gal./WD tank	200	5.3	8.3	75
Motive water		3,320 gal./WD tank	0	0		
Area leak/ overflow		122,731 gal./day	6.4	3.0		
WS	1 building					
Process water		40,000 gal./WD tank	13.2	2.0	2.0	18
CO						
Process water	---	~30,000 gal./yr	110	0.034 kg/day	0.034 kg/day	nil

Total for one DNT WD tank/day = 11.1 kg/WD tank.
0.28 kg/1,000 lb propellant.

Table 6. DNT analyses on daily BWTP samples (mg/L)

Date	Raw Composite	Raw	New RBC Influent	Old RBC Influent	Old RBC Effluent	Plant Effluent
10-17-89	17	32	8	3	1.0	0.8
10-18-89	16	23	11	4	0.4	0.2
10-19-89	15	5	11	6	1.5	1.2
10-20-89	6	3	ND	ND	ND	ND
10-21-89						
10-22-89						
10-23-89	9	11	4	1	ND	ND
10-24-89	11	6	2	1	ND	ND
10-25-89	8	9	2	0	ND	ND
10-30-89	11.3	16.9	4.1	1.1	ND	ND
10-31-89	7.7	32.2	ND	ND	ND	ND
11-01-89	10.0	13.3	3.0	ND	ND	ND
11-02-89	3.9	3.9	1.4	0.8	ND	ND
11-03-89	3.6	2.2	0.9	0.0	trace	0.2
11-06-89	3.9	3.9	0.2	0.1	0.1	0.1
11-07-89	12.4	4.3	0.4	0.4	0.3	0.4
11-08-89	2.6	4.1	ND	ND	ND	ND
11-09-89	4.2	2.7	0.1	0.1	0.1	0.1
11-10-89	4.2	2.9	0.4	0.2	0.6	0.1

ND = none detected

Average influent DNT concentration = 7.67 mg/L
Average effluent DNT concentration = 0.16 mg/L
Removal efficiency = 98%

Table 7. COD analyses on daily BWTP samples (mg/L)

Date	Raw Composite	Raw	New RBC Influent	Old RBC Influent	Old RBC Effluent	Plant Effluent
10-17-89	192	397	110	88	85	83
10-18-89	175	288	99	71	69	71
10-19-89	107	132	79	52	43	48
10-20-89						
10-21-89	297	129	89	63	49	47
10-22-89	731	554	250	200	168	132
10-23-89	819	334	353	236	191	192
10-24-89	255	107	176	120	71	81
10-25-89	167	178	114	89	66	62

Average influent COD = 343
Average effluent COD = 89.5
Removal efficiency = 74%

Table 8. Statistics for RAAP BWTP effluent

	1989								1990				Minimum	Maximum for year	Average for year
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr			
Flow (MGD)															1.28
Avg	1.26	.912	.942	1.11	1.04	1.05	1.12	1.76	1.83	1.79	1.45	1.12			
Max	1.87	1.43	1.71	1.65	2.20	1.63	1.69	2.56	2.15	2.[illegible]	3.09	2.61		3.09	
pH															
Min	7.50	7.30	6.90	7.50	7.70	7.50	7.10	7.10	7.50	7.30	7.30	7.00	6.90		
Max	8.40	8.40	8.30	8.20	8.70	8.30	8.00	7.90	7.90	7.90	8.00	7.90		8.70	
BOD5															
Load (kg/day)															111.69
Avg	214.28	56.59	73.65	43.62	65.13	59.55	241.38	203.92	56.07	67.95	190.76	66.17			
Max	383.52	66.25	90.79	61.24	115.58	88.64	623.42	265.82	71.40	157.32	612.27	115.58		623.42	
Conc (mg/L)															23.00
Avg	46.05	18.89	21.65	10.45	17.70	18.13	46.53	29.30	8.35	9.27	35.42	14.23			
Max	74.00	22.65	30.00	13.50	28.00	23.20	97.00	40.80	10.30	18.60	99.00	22.30		97.00	
TSS															
Load (kg/day)															201.87
Avg	189.60	162.71	109.26	129.39	183.46	78.90	514.94	234.68	107.09	249.29	194.02	181.14			
Max	279.87	329.10	203.60	161.16	390.08	171.94	1606.75	310.29	329.49	400.94	392.91	342.08		1606.70	
Conc (mg/L)															43.17
Avg	43.40	39.00	26.80	31.25	53.60	43.00	96.45	33.30	29.12	36.60	44.80	36.75			
Max	64.00	74.00	45.00	42.00	81.00	56.00	250.00	46.00	49.00	64.00	74.00	66.00		250.00	
COD															
Load (kg/day)															388.52
Avg	515.40	318.94	166.02	184.68	260.82	192.17	987.36	619.85	203.33	359.04	654.24	191.41			
Max	984.70	459.23	208.63	317.51	390.08	275.10	2834.30	762.27	262.25	642.81	1148.72	367.97		2834.30	
Conc (mg/L)															79.81
Avg	110.25	98.50	44.60	46.25	71.25	60.00	191.00	90.20	30.00	51.00	121.25	41.00			
Max	190.00	157.00	62.00	70.00	107.00	72.00	441.00	117.00	39.00	76.00	222.00	71.00		441.0	

Table 8. (cont)

	1989								1990					Maximum	Average
	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	Minimum	for year	for year
SO4															
Load (kg/day)															
Avg	1944.92	1408.77	1359.25	2468 78	1901 77	1299 04	1253 46	726 02	1780 61	1837 75	1324 89	951 37			1521 37
Max	2555 71	2112.48	2349 26	3628 68	2311 58	1795 80	2120 90	1406 38	2076 12	2132 70	1479 01	1644.20		3628 68	
Conc (mg/L)															
Avg	420 00	438.26	349.00	890 00	516 00	367 00	287 50	108 00	266 00	260.00	245.00	221 25			338.70
Max	530.00	500.00	490.00	600.00	580 00	470 00	340 00	240 00	300 00	340 00	270 00	378.00		800 00	
N															
Load (kg/day)															
Avg	19.69	71.64	120 92	102 15	86 58	100 55	18 01	31 92	179 01	125 07	24 89	79.61			80.00
Max	52.01	151 87	199 43	165 56	132 77	160 09	29 29	78 59	287 69	178 22	67 60	144 69		287 69	
Conc (mg/L)															
Avg	3 84	20.16	31 57	24.30	23 87	26 78	5 84	4 68	26 58	19 89	4 83	16 62			17.58
Max	8.75	34.16	46 00	38.50	38 76	41 90	14 34	10 98	40 00	29 83	13.49	33 00		46.00	
DNT															
Load (kg/day)															
Avg	0 00	.064	0.00	0.00	0.00	1 26	0 03	4 74	12 98	.66	0 07	.05			1.65
Max	0 00	.216	0.00	0.00	0 00	2 83	145	24 25	26 70	2 03	0 35	.26		26.70	
Conc (mg/L)															
Avg	0.00	.019	0.00	0.00	0 00	.28	.0075	71	1 93	.07	0.14	.013			.264
Max	0.00	.074	0 00	0.00	0 00	.74	.03	2 50	3 60	24	0 07	.05		3 60	

Table 9. DNT biomass/bioreactor study

	Blank reactor			DNT supplemented reactor		
Time (days)	Conc DNT (mg/L)	COD (mg/L)	Unknown peaks (min)	Conc DNT (mg/L)[i]	COD (mg/L)	Unknown peaks (min)
0	0.0	37		3.0	424	
1	0.0	1		9.6	32	3.53[e], 3.79[g], 5.68[h]
2[a]						
3[a]						
4	0.0	190		0.0	66	2.72[b], 2.99[c], 3.82[g]
5[a]						
6	0.0	260		0.1	94	2.86[c], 3.11[d], 3.56[e]
7	0.1	179		1.2	67	2.54[b], 3.02[c], 3.70[g]
8	0.7	212	5.46[h]	1.0	292	2.48[b]
9[a]						
10[a]						
11	0.0	55	2.96[c]	10.6	497	
12	0.1	47	5.42[h]	0.0	375	3.63[f]
13	0.0	50		0.0	275	
14	0.0	203		0.0	425	
15	0.0	232		0.0	359	

[a] No wastewater or DNT replacement
[b] unknown 1
[c] unknown 2
[d] unknown 3
[e] unknown 4
[f] unknown 5
[g] unknown 6
[h] contaminant from wastewater
[i] Leakage from replenishment of DNT to supplemented reactor.

Table 10. Biodegradation test no. 1

	Biological oxygen demand (mg/L)							
Time (h)	100% seed	Blank	Vessel 1	Vessel 2	Vessel 3	Vessel 4	Vessel 5	Vessel 6
0	0	0	0	0	0	0	0	0
7	20	50	70	70	60	60	50	50
23	280	270	190*	230	230	220	200	210
29	290	280	210	280	270	260	240	250
77	280	600	460	490*	470	450	490	490
95	280	680	560	545	520*	500	540	540
101	280	700	570	555	530	510	560	560
119	320	840	730	685	760	580*	680	680
144	340	870	750	685	800	540	690*	690
168	360	900	780	705	820	580	710	690*
0	DNT 0	DNT 0	DNT 70.9	DNT 70.9	DNT 70.9	DNT 70.9	DNT 70.9	DNT 70.9
	COD 1471							
23			DNT 24.7					
			COD 224					
77				DNT 0				
				COD 219				
95					DNT 0			
					COD 208			
119						DNT 0		
						COD 140		
144							DNT 0	
							COD 170	
168		DNT 0	DNT 0	DNT 0	DNT 0	DNT 0	DNT 0	DNT 0
		COD 68	COD 90	COD 92	COD 82	COD 70	COD 76	COD 140

*Indicates respirometer opened and ~10 mL sample removed for HPLC chromatographic analysis.
Note: DNT and COD concentrations are in mg/L.

Table 11. Peak analysis of biodegradation test no. 1

	Peak residence time (min)											
Time (h)	1.3[b]	1.7[a]	1.8[a]	1.85[a]	2.0[a]	2.4[b]	2.9[b]	3.8[b]	4.0[b]	6.0[b]	7.4[b]	8.4[b]
0										5.88		
23			1.77	1.95	2.07			3.86		6.08	7.45	8.42
77	1.34			1.87			2.85	3.75	4.03			
95		1.63	1.84		1.98	2.45	2.95	3.80	4.02			
119		1.74		1.87	2.00	2.42		3.82	4.02			
144	1.34		1.80	1.84	2.03	2.41		3.78				
168		1.67	1.81		1.97	2.40						
100% seed		1.64		1.94								

[a] Compounds related to biomass.
[b] ONT byproducts.

Table 12. Biodegradation test no. 2

	Biological oxygen demand (mg/L)								
Time (h)	100% seed	Blank	Vessel 1	Vessel 2	Vessel 3	Vessel 4	Vessel 5	Vessel 6	Vessel 7
0	0	0	0	0	0	0	0	0	0
22	400	150	130	170	190	180	160	220	170
28	520	180	140	200	220	220	190	250	190
94	520	370	270	440	460	440	400	440	330
118	520	470	320	530	520	500	450	550	470
142	520	490	340	560	580	570	520	550	500
166	520	570	360	600	620	620	550	560	520
190	520	570	380	610	640	620	560	570	550
264	520	610	460	740	760	720	680	710	660
	Degradation of DNT (mg/L)								
0	0	0	70.9	70.9	70.9	70.9	70.9	70.9	70.9
22			0.08						
28									
94					0				
118						0			
142							0		
166								0	
190									0
264		0	0	0	0	0	0	0	0

Table 13. Biodegradation test no. 3

	Biological oxygen demand (mg/L)								
Time (h)	100% seed	Blank	Vessel 1	Vessel 2	Vessel 3	Vessel 4	Vessel 5	Vessel 6	Vessel 7
0	0	0	0	0	0	0	0	0	0
5	80	35	40	45	50	40	45	40	50
24	200	210	210	220	220	210	220	240	230
31	240	250	300	270	280	260	270	250	260
3	230	360	420	380	380	360	400	360	370
5	240	400	450	410	410	390	430	390	400
7	240	480	530	530	490	470	500	460	480
10	240	540	610	600	550	520	560	480	530
17	240	580	680	710	620	600	650	610	630
192	240	610	690	740	620	630	660	620	630
216	240	610	700	750	620	670	660	620	640
245	240	610	700	750	620	710	710	620	640
264	240	610	700	760	630	830	710	620	640
337	250	610	710	790	630	840	770	770	640
	Degradation of DNT (mg/L)								
0	0	35	35.4	35.49	35.49	35.4	35.4	35.4	35.4
24			0						
48				0					
77					0				
170						0			
216							0		
264								0	
337		0	0	0	0	0	0	0	0

Table 14. Laboratory results for UV, ozone, hydrogen peroxide experiments

	DNT concentration (mg/L)					
Time (min)	UV (5mW/cm^2)	Ozone (unknown)	Hydrogen peroxide (3%)	UV/hydrogen peroxide (5mW/cm^2) (1%)	UV/ozone (5mW/cm^2) (unknown)	UV/ozone on actual wastewater
0	154	186	160	185	189	126
0.5	---	---	---	---	---	120
1	155	---	---	---	137	115
2	153	---	---	---	---	---
2.5	---	---	---	---	---	111
3	153	177	---		5	---
4	---	---	---	---	---	---
5	156	---	---	---	3	89
7	157	173	---	---		
10	152	---	---	140		
14	150	---	---	---		
15	---	155	---	---		
20	159	---	149	85		
30	---	128	---	---		
40	---	---	---	45		
60	138	---	---	---		

Table 15. Optimization of time

Time (min)	WH FS-400 (mg)	Concentration (mg/L)*	% Concentration remaining
0	---	219	100
60	20.3	177	80.8
120	22.6	138	63.0
150	21.6	151	68.9
180	26.0	151	68.9
210	20.7	132	60.3
240	20.5	133	60.7

*All concentrations have been normalized to reflect adsorption by a 20-mg sample of FS-400.

Table 16. Adsorption isotherm for water dry water

Wt FS-400 (g)	Final concentration DNT (mg/L)	X/M (mg DNT/g FS-400)
---	229	---
0.0257	177	202.3
0.0521	138	174.7
0.0774	100	166.7
0.1038	70	153.2
0.1286	60	131.4
0.1606	33	122.0
0.2019	10	108.5
0.2512	7	88.4

Table 17. Adsorption isotherm for solvent-fortified water dry water

Wt. FS-400 (g)	Ether, %	Alcohol (%)	DNT (mg/L)	X/M (mg DNT/g FS-400)
---	0.610	1.485	168	---
0.0304	0.303	1.466	154	46.1
0.0496	0.339	1.458	118	100.8
0.0776	0.389	1.457	93	96.6
0.0993	0.381	1.461	72	102.9
0.1245	0.310	1.466	44	99.6
0.1503	0.218	1.459	38	86.5
0.2078	0.320	1.482	17	72.7
0.2506	0.237	1.490	10	63.0

Table 18. Adsorption isotherm for plant effluent with DNT

Wt. FS-400 (g)	DNT (mg/L)	X/M (mg DNT/g FS-400)
---	1.327	---
0.0116	1.123	1.759
0.214	1.021	1.430
0.0321	0.802	1.636
0.0507	0.502	1.627

Table 19. Test matrix for DNT degradation by UV/ozonation[1]

Test No.	Desired DNT conc (mg/L)	UV bulb type	Ozone flow rate (SCFM)	Solvents in water (wt %)
1	100	low	0	0
2	100	low	0	0
3	100	low	0	0
4	100	low	5	0
5	100	low	5	0
6	100	low	5	0
7	100	low	10	0
8	100	low	10	0
9	100	low	10	0
10	100	low	15	0
11	100	low	15	0
12	100	low	15	0
13[2]	100	high	10	0
14[2]	100	high	10	0
15[2]	100	high	10	0
16	100	optimum	0	2.0 wt % ether, 2.0% ethyl alcohol
17	100	optimum	0	2.0 wt % ether, 2.0% ethyl alcohol
18	100	optimum	0	2.0 wt % ether, 2.0% ethyl alcohol
19	100	optimum	5	2.0 wt % ether, 2.0% ethyl alcohol
20	100	optimum	5	2.0 wt % ether, 2.0% ethyl alcohol
21	100	optimum	5	2.0 wt % ether, 2.0% ethyl alcohol
22	100	optimum	10	2.0 wt % ether, 2.0% ethyl alcohol
23	100	optimum	10	2.0 wt % ether, 2.0% ethyl alcohol
24	100	optimum	10	2.0 wt % ether, 2.0% ethyl alcohol
25	100	optimum	15	2.0 wt % ether, 2.0% ethyl alcohol
26	100	optimum	15	2.0 wt % ether, 2.0% ethyl alcohol
27	100	optimum	15	2.0 wt % ether, 2.0% ethyl alcohol
28	wastewater	optimum		
29	wastewater	optimum		
30	wastewater	optimum		

[1]Additional testing will be performed as determined necessary for economic and design requirements

[2]Testing with the high pressure bulb will be expanded if results are successful.

Table 20. Operating conditions for activated carbon studies

Test No.	Activated carbon	DNT (mg/L)	Step	Flow rate (mL/min)	Total volume (bed volume)	Direction of flow	Elution solvent (% by wt)
1	FS-400	0 100[1] 0	backwash exhaustion elution	0.75 3.0 3.0	2-1/2 ? ?	up down down	0 ? 2% ethyl alcohol 2% ether
2	FS-400	0 100[1] 0	backwash exhaustion elution	0.75 3.0 3.0	2-1/2 ? ?	up down down	0 ? 2% ethyl alcohol 2% ether
3	FS-400	0 100[1] 0	backwash exhaustion elution	0.75 3.0 3.0	2-1/2 ? ?	up down down	0 ? 2% ethyl alcohol 2% ether
4	FS-400	0 100[1]	backwash exhaustion	0.75 3.0	2-1/2 ?	up down	0 2% ethyl alcohol 2% ether
5	FS-400	0 100[1]	backwash exhaustion	0.75 3.0	2-1/2 ?	up down	0 2% ethyl alcohol 2% ether
6	FS-400	0 100[1]	backwash exhaustion	0.75 3.0	2-1/2 ?	up down	0 2% ethyl aclohol 2% ether

[1] 100 mg/L in wastewater.

Table 21. GAC column prior to breakthrough

Run day	Influent processed (L/day)	Influent (mg/L)					Effluent (mg/L)				
		DNT	Ether	Alcohol	DPA	DBP	DNT	Ether	Alcohol	DPA	DBP
0	0.0	150.2									
1	7.0	137.3					ND				
2	3.67										
3	3.67	132.3					ND				
4	3.67	156.3					ND				
5	3.0	273.2					ND				
6	5.0	259.3					ND				
7	5.0	265.0					ND				
8	6.67										
9	6.67										
10	6.67	286.8	133	513			ND	68	578		
11	6.0	283.9	214	624			ND	86	618		
12	5.0	255.5	147	564			ND	47	544		
13	5.0	244.6	ND	ND			ND	ND	ND		
14	3.0	219.7	230	3030			ND	ND	1800		
15	0.75										
16	0.75										
17	0.75						ND				
18	0.75	207.6	70	3030			ND	80	3020		
19	5.0										
20	5.0	187.8	150	2580			ND	ND	2450		
21	5.0	187.1	ND	2340			ND	ND	2270		
22	0.0										
23	0.0										
24	0.0										
25	0.0										
26	0.0										
27	0.0										

Table 21. (cont)

Run day	Influent processed (L/day)	Influent (mg/L)					Effluent (mg/L)				
		DNT	Ether	Alcohol	DPA	DBP	DNT	Ether	Alcohol	DPA	DBP
28	0.0										
29	0.0										
30	0.0										
31	0.0										
32	5.0	360	ND	ND			ND				
33	5.0	---					ND				
34	1.0	206.6					ND				
35	4.5	128.7					ND				
36	0.67										
37	0.67										
38	0.67										
39	6.5	205.3					ND				
40	8.0	194.0					ND				
41	4.0	189.8	ND	300	2.16		ND	ND	480	1.58	
42	4.5	102.6					ND				
43	5.0										
44	5.0										
45	5.0	111	ND	160			ND	ND	100		
		170	100	340							
46	3.75										
47	3.75	161					ND				
48	2.5										
49	6.0										
50	6.0										
51	6.0										
52	6.0										
53	3.0	209	ND	420			ND	90	410		
54	5.0	214	ND	370			ND	ND	470		
55	10.0										

Table 21. (cont)

Run day	Influent processed (L/day)	Influent (mg/L)					Effluent (mg/L)				
		DNT	Ether	Alcohol	DPA	DBP	DNT	Ether	Alcohol	DPA	DBP
56	0.0	227	80	440	0.49	ND	ND	ND	410	ND	ND
		148.6	ND	460	1.523						
57	13.5										
58	7.25										
59	7.25	151	ND	50	1.35	ND	ND	ND	230	ND	ND
		107	ND	35	1.48	ND					
60	17.5	115	ND	310							
		248	100	190	2.39	ND	ND	ND	350		
61	11.5	203.7	160	ND			ND	ND	90		
62		230.9	60	170			ND	90	60		
		271.0	150	100							
63	8.5	257.8	60	ND	2.05	ND	ND	ND	30	ND	ND
64	15.5										
65	9.5										
66	9.5	180.3	ND	20	2.05	ND	ND	70	70	ND	ND
		127.2	ND	ND	2.06	ND					
67	11.5	117.5	ND	20			ND	ND	ND		
68	4.0	119.2									
		278.6	250	300	3.92	ND	ND				
69	6.0										
	6.0										
Mean			68	584.5				26.6	69.9		
Standard deviation			81.7	925.2				38.1	91.0		

Table 22. GAC column after breakthrough

			Concentration (mg/L)				
Run day	Aliquot No.	Aliquot vol (L)	DNT	Alcohol	Ether	DPA	DBP
69*	1	500	3.4	240	ND	ND	ND
	2	500	3.4	230	ND	ND	ND
	3	500	3.2	190	ND	ND	ND
	4	500	4.0	160	ND	ND	ND
	5	500	5.1	200	ND	ND	ND
	6	500	5.1	190	ND	ND	ND
	7	500	5.8	230	ND	ND	ND
	8	500	6.8	310	ND	ND	ND
	9	500	7.4	300	ND	ND	ND
	10	500	8.8	250	60	ND	ND
	11	500	7.3	240	ND	ND	ND
	12	500	8.9	220	ND	ND	ND
	13	500	11.1	280	80	ND	ND
	14	500	10.4	290	70	ND	ND
	15	500	11.3	280	ND	ND	ND
	16	500	10.0	300	ND	ND	ND
	17	500	8.9	160	ND	ND	ND
	18	500	7.7	310	ND	ND	ND
	19	500	6.6	310	80	ND	ND
	20	500	4.6	300	ND	ND	ND
	21	500	5.2	300	60	ND	ND
	22	500	4.5	320	70	ND	ND
	23	150*	4.6	290	ND	ND	ND
70	24	500	4.6	310	90	ND	ND
	25	500	4.3	280	ND	ND	ND
	26	500	4.8	210	ND	ND	ND
	27	500	5.1	160	ND	ND	ND

Table 22. (cont)

			Concentration (mg/L)				
Run day	Aliquot No.	Aliquot vol (L)	DNT	Alcohol	Ether	DPA	DBP
	28	500	5.5	210	ND	ND	ND
	29	500	2.9	190	70	ND	ND
	30	500	5.5	140	ND	ND	ND
	31	500	6.9	280	60	ND	ND
	32	500	7.5	300	ND	ND	ND
	33	500	7.7	130	ND	ND	ND
	34	500	8.0	320	90	ND	ND
	35	500	4.1	280	ND	ND	ND
	36	500	9.4	310	ND	ND	ND
	37	500	9.7	200	ND	ND	ND
	38	500	10.5	190	70	ND	ND
	39	500	11.7	170	80	ND	ND
	40	500	12.3	110	80	ND	ND
	41	500	13.6	320	90	ND	ND
	42	500	14.8	310	80	ND	ND
	43	500	14.9	340	80	ND	ND
	44	500	16.9	290	60	ND	ND
	45	500	18.4	290	70	ND	ND
	46	200*	17.7	280	70	ND	ND
71[b]	1	500	25.9	12,750	250	ND	ND
	2	500	38.0	13,570	1,750	ND	ND
	3	500	38.5	13,470	990	ND	ND
	4	500	37.0	13,630	1,060	ND	ND
	5	500	38.4	13,540	500	ND	ND
	6	500	37.5	13,670	1,360	ND	ND
	7	500	38.8	13,790	1,040	ND	ND
	8	500	38.1	13,860	2,270	ND	ND

Table 22. (cont)

			Concentration (mg/L)				
Run day	Aliquot No.	Aliquot vol (L)	DNT	Alcohol	Ether	DPA	DBP
	9	500	36.2	13,800	1,780	ND	ND
	10	500	33.4	13,560	1,780	ND	ND
	11	500	29.2	12,280	290	ND	ND
	12	500	26.0	12,120	ND	ND	ND
	13	300*	18.11	11,210	110	ND	ND
72	14	500	18.8	11,540	1,430	ND	ND
	15	500	20.0	13,150	1,540	ND	ND
	16	500	19.7	13,460	1,970	ND	ND
	17	500	23.2	13,350	1,880	ND	ND
	18	500	28.1	12,950	590	ND	ND
	19	500	29.0	13,200	910	ND	ND
	20	500	32.1	13,280	1,160	ND	ND
	21	500	34.5	12,920	460	ND	ND
	22	250*	39.8	12,890	120	ND	ND
73[c]	1	500	35.4	9,190	490	ND	ND
	2	500	36.0	6,730	ND	ND	ND
	3	500	38.3	7,170	820	ND	ND
	4	500	43.0	7,140	700	ND	ND
	5	500	47.8	7,180	850	ND	ND
	6	500	55.0	7,090	660	ND	ND
	7	500	57.6	7,200	840	ND	ND
	8	500	63.5	7,120	540	ND	ND
	9	500	64.5	7,070	940	ND	ND
	10	500	67.2	6,780	540	ND	ND
	11	500	70.5	6,740	600	ND	ND
	12	500	74.0	6,780	730	ND	ND
	13	500	72.3	6,770	480	ND	ND

Table 22. (cont)

			Concentration (mg/L)				
Run day	Aliquot No.	Aliquot vol (L)	DNT	Alcohol	Ether	DPA	DBP
	14	500	76.0	6,870	1,180	ND	ND
	15	500	80.6	6,690	590	ND	ND
	16	500	82.7	6,560	580	ND	ND
	17	350*	88.2	6,750	270	ND	ND
74	18	500	92.9	6,410	ND	ND	ND
	19	500	92.1	6,360	40	ND	ND
	20	500	93.5	6,390	420	ND	ND
	21	500	101.7	6,460	420	ND	ND
	22	500	102.2	6,300	210	ND	ND
	23	500	107.0	---	400	ND	ND
	24	500	118.9	6,250	140	ND	ND
	25	500	109.3	6,610	490	ND	ND
	26	500	115.0	6,450	230	ND	ND
	27	500	105.4	7,050	410	ND	ND
	28	500	106.0	7,120	340	ND	ND
	29	500	106.4	7,160	660	ND	ND
	30	500	95.1	6,860	230	ND	ND
	31	440*	91.7	6,790	180	ND	ND
75	32	500	---	6,470	80	ND	ND
	33	500	111.8	6,650	290	ND	ND
	34	500	117.4	6,390	190	ND	ND
	35	500	124.4	6,410	ND	ND	ND
	36	500	125.0	6,500	160	ND	ND
	37	500	126.5	6,520	110	ND	ND
	38	500	132.2	6,450	80	ND	ND
	39	500	130.2	6,260	ND	ND	ND
	40	500	140.4	6,470	90	ND	ND

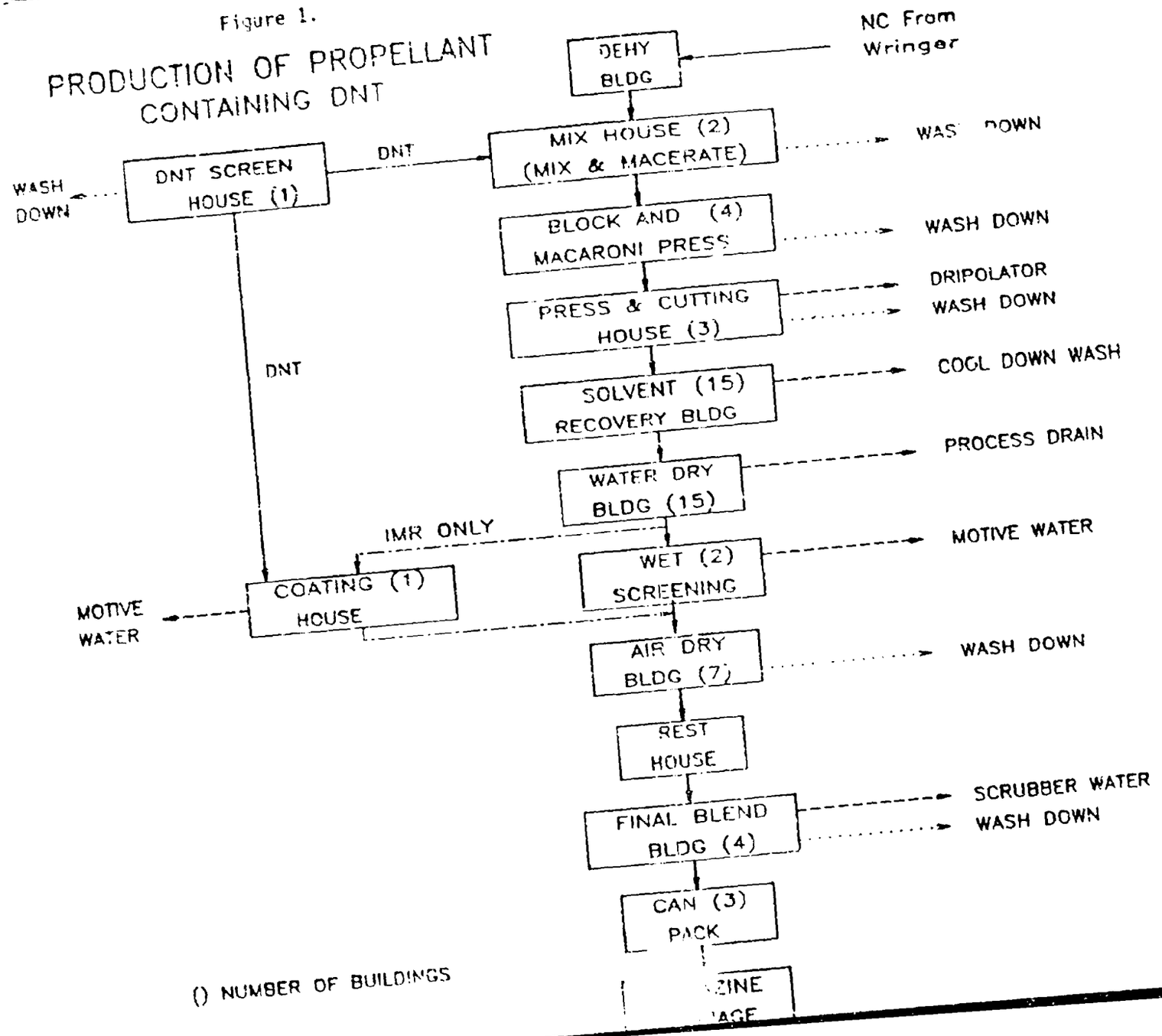
Table 22. (cont)

			Concentration (mg/L)				
Run day	Aliquot No.	Aliquot vol (L)	DNT	Alcohol	Ether	DPA	DBP
	41	500	136.3	6,410	160	ND	ND
	42	500	134.6	6,260	ND	ND	ND
	43	500	132.3	5,590	ND	ND	ND
	44	500	133.1	5,570	140	ND	ND
	45	500	133.2	5,270	ND	ND	ND
	46	500	129.3	4,460	ND	ND	ND
	47	500	122.3	5,110	ND	ND	ND
	48	500	121.9	4,960	ND	ND	ND
	49	500	122.4	5,250	80	ND	ND
	50	390*	113.4	5,270	110	ND	ND

[a] Period following breakthrough.
[b] Solvent addition.
[c] Solvent reduction.
* Last sample in fraction collector.

Figure 1.

PRODUCTION OF PROPELLANT CONTAINING DNT



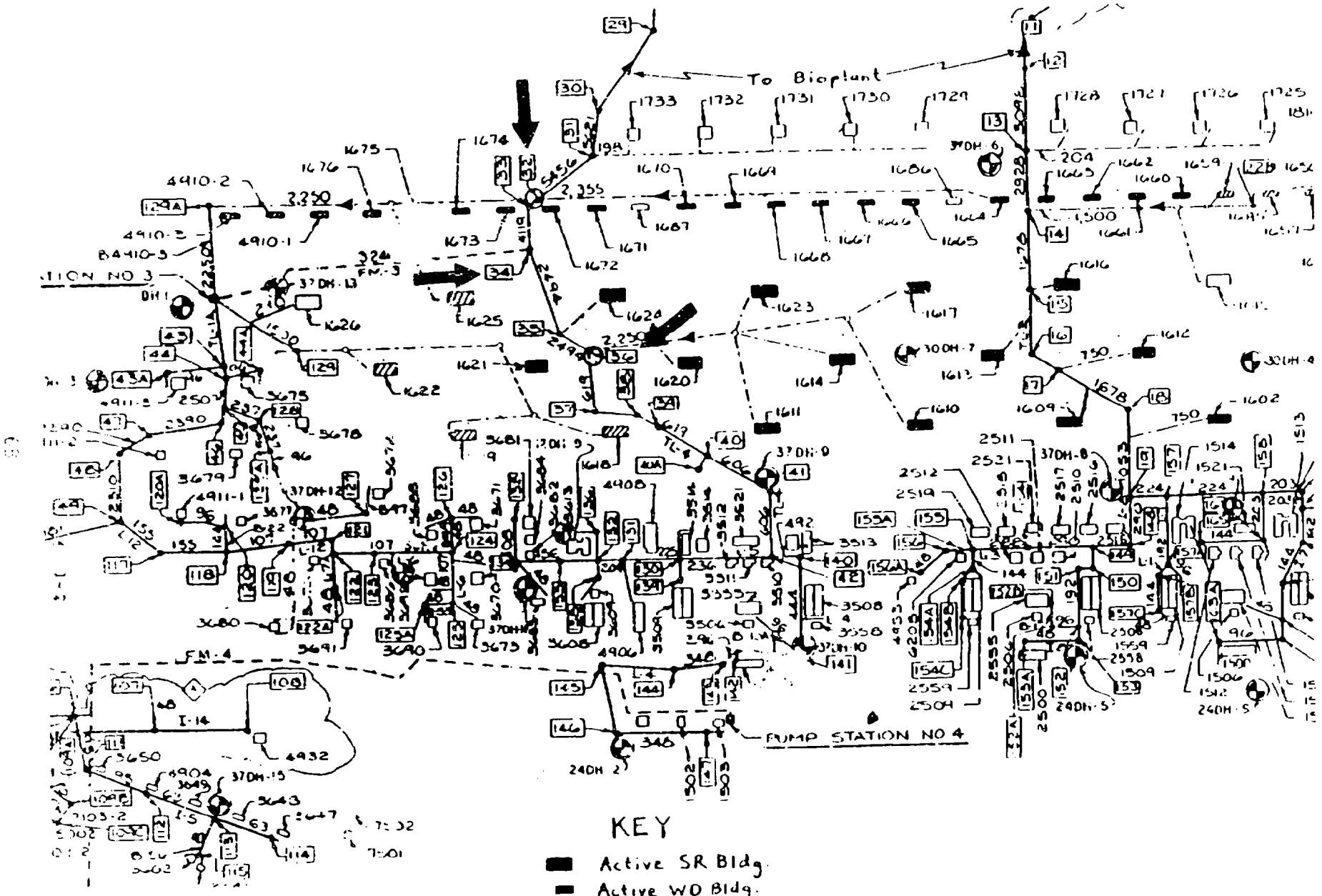


Fig. 2 ... SR ... WD ... ldg...

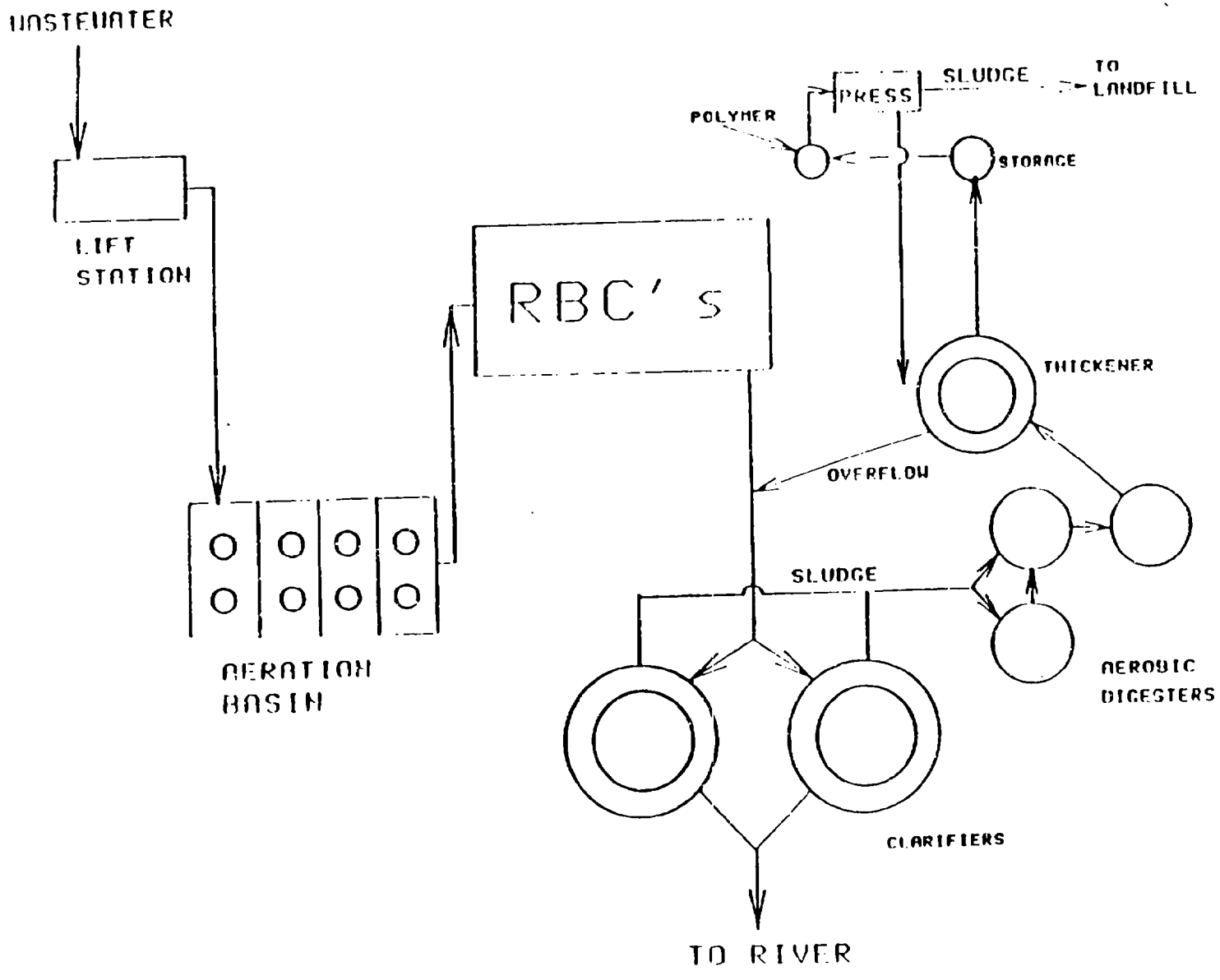


Figure 3. Bioplant

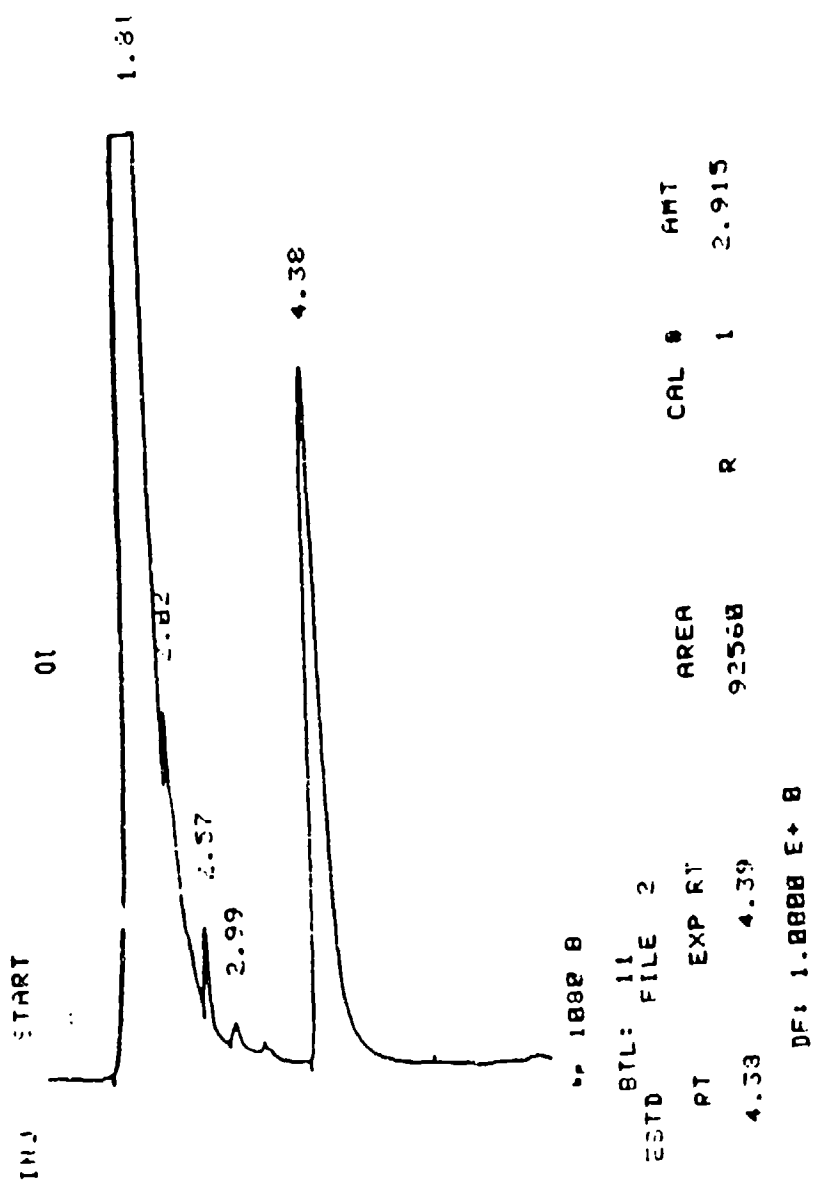


Figure 4. HPLC chromatogram of raw influent to the equalization basin

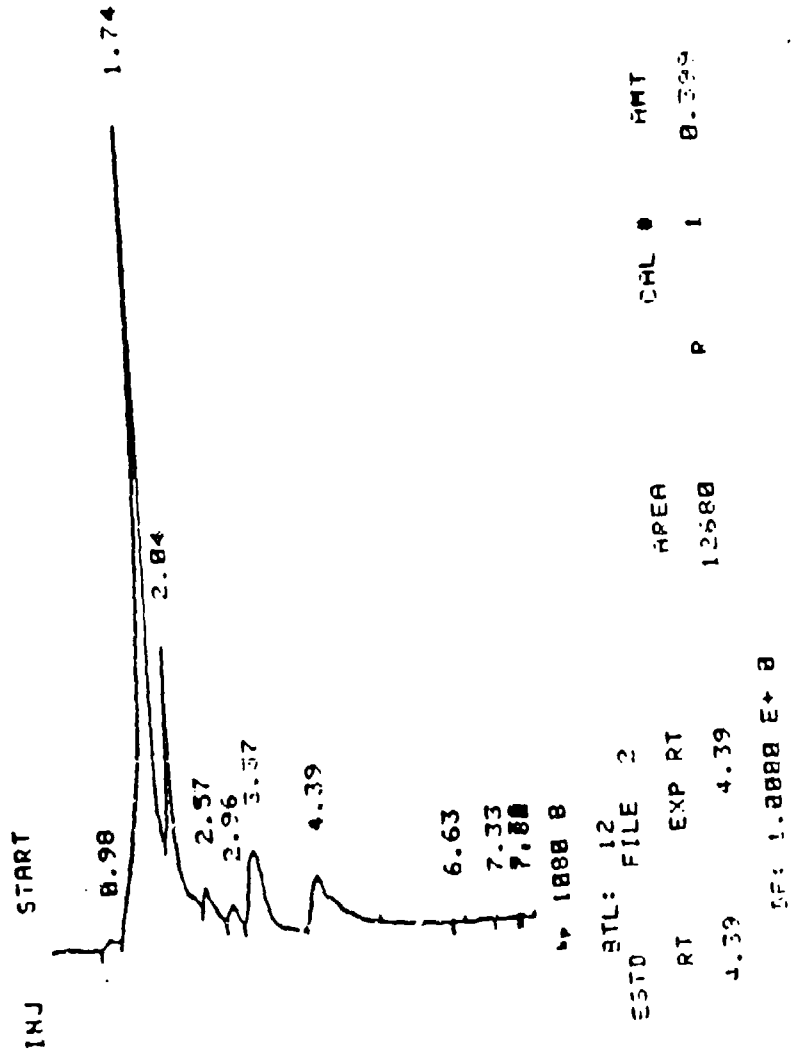


Figure 5. HPLC chromatogram of raw influent to the new RBC's

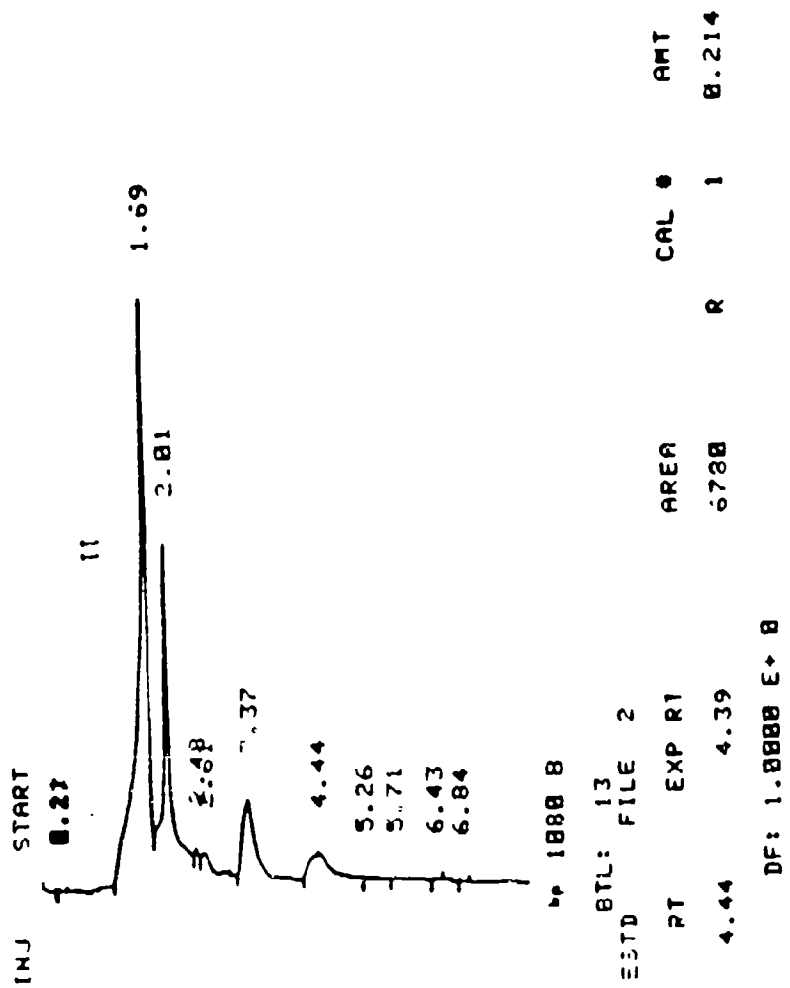


Figure 6. HPLC chromatogram of influent to old RBC's

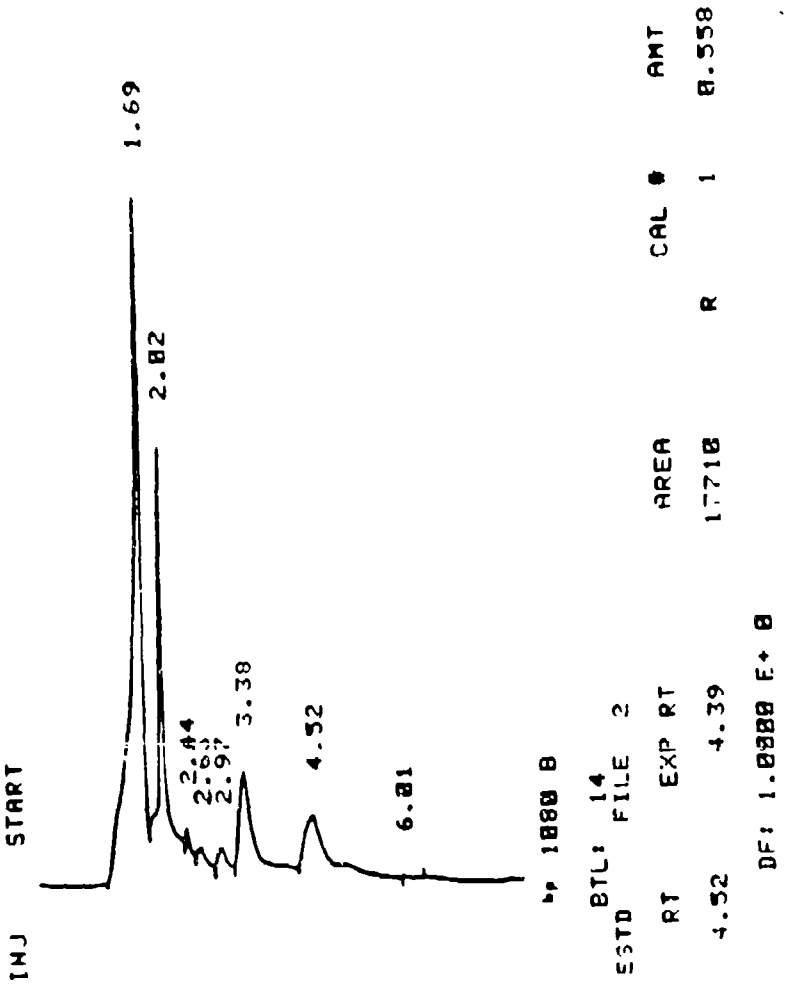


Figure 7. HPLC chromatogram of effluent from old RBC's

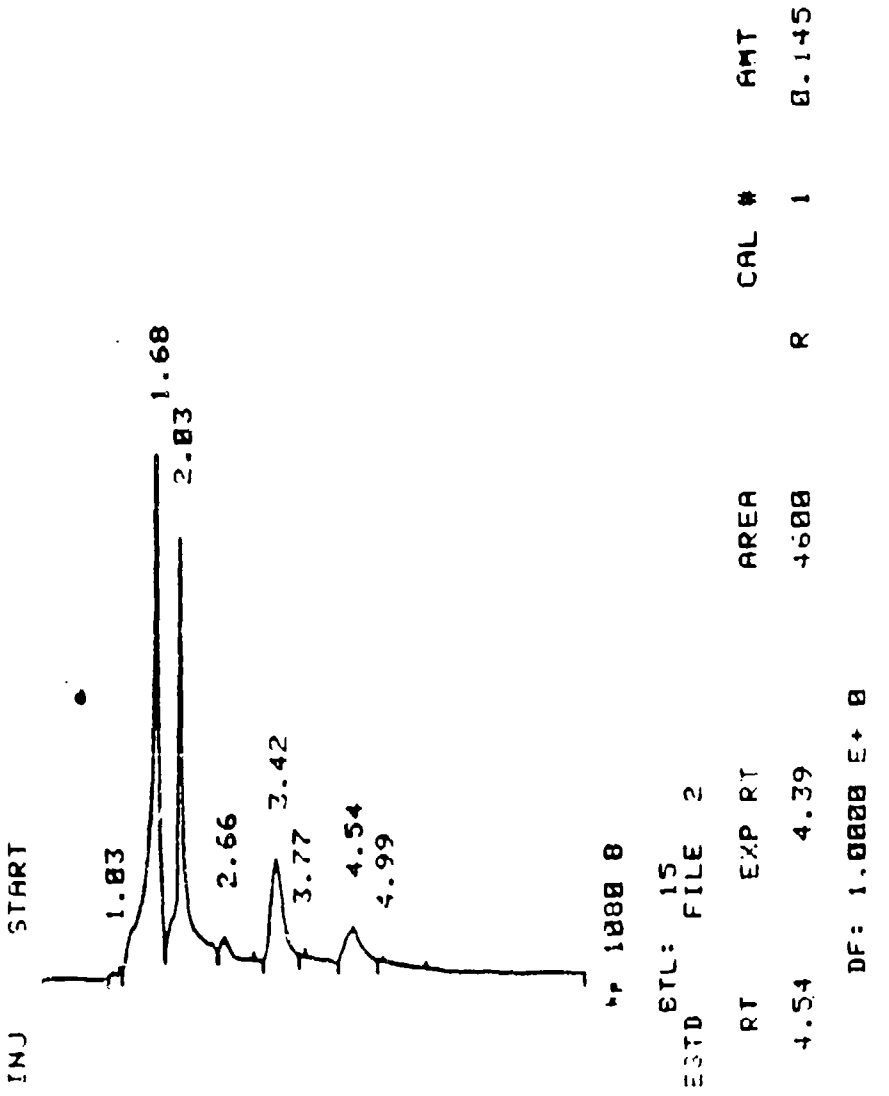


Figure 8. HPLC chromatogram of clarified effluent

Figure 9.

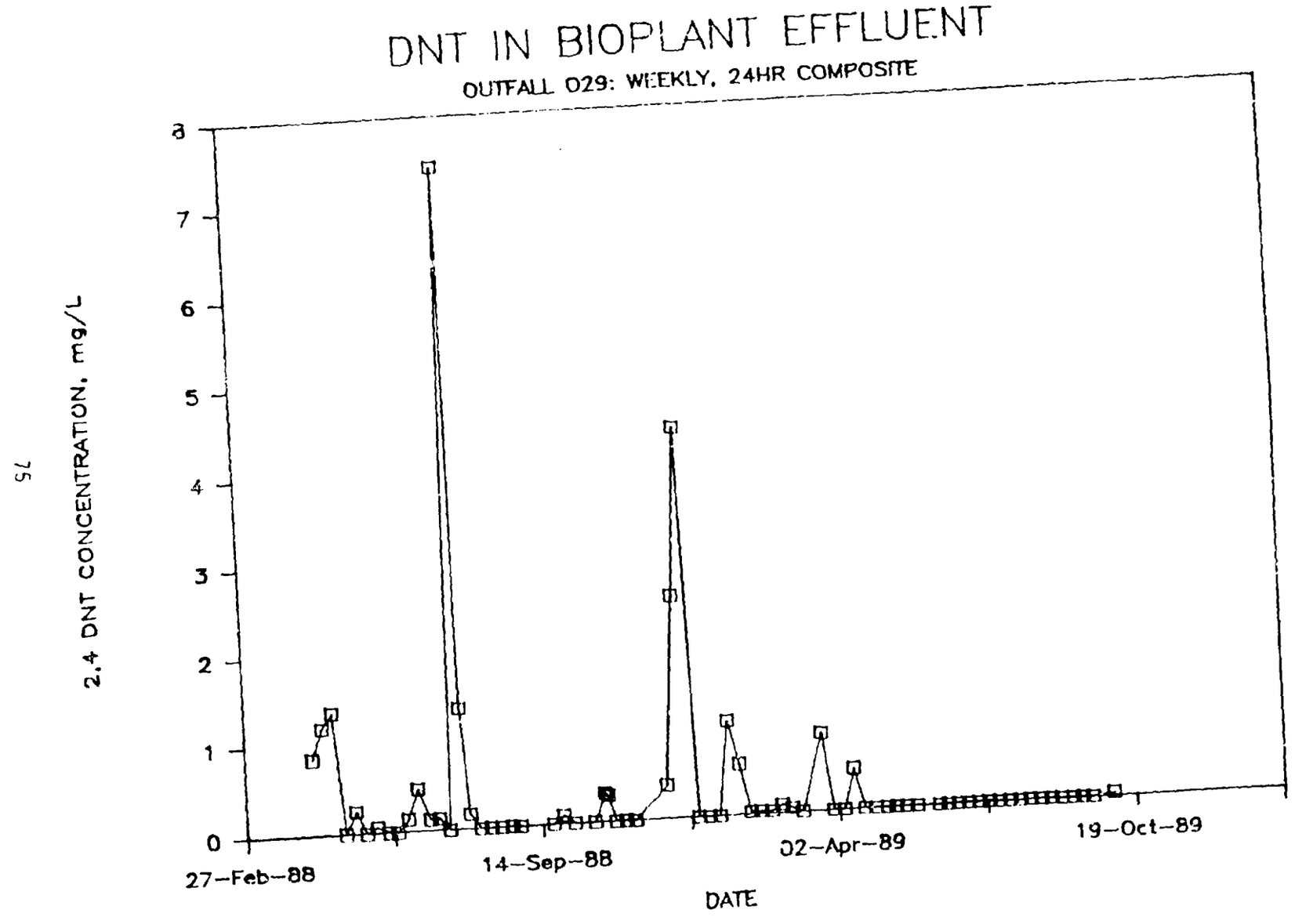
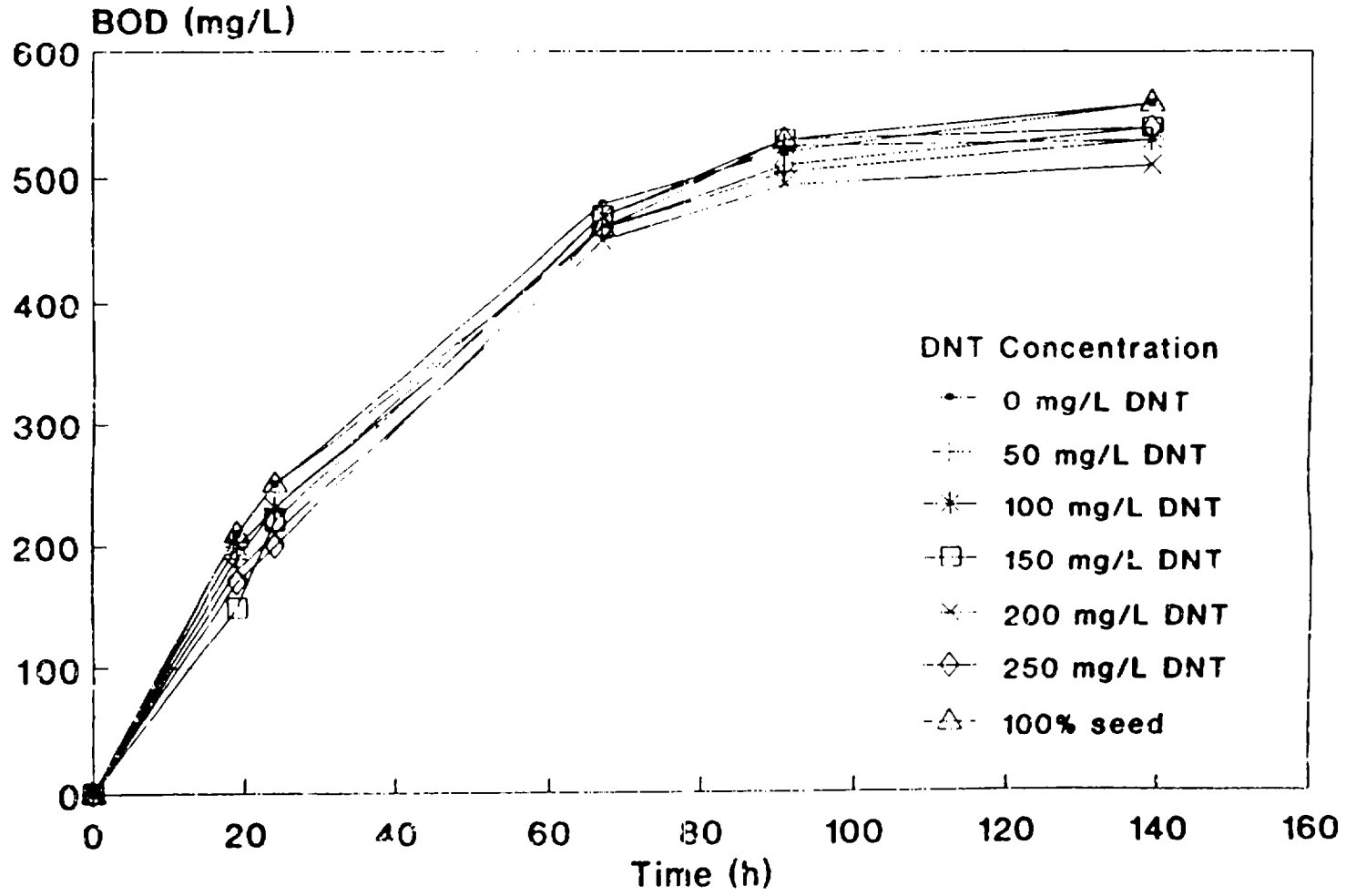

DNT IN BIOPLANT EFFLUENT
OUTFALL 029: WEEKLY, 24HR COMPOSITE
2,4 DNT CONCENTRATION, mg/L
8
7
6
5
4
3
2
1
0
27-Feb-88
14-Sep-88
02-Apr-89
19-Oct-89
DATE

Figure 10

RESPIROMETER TOXICITY DATA FOR DNT

Test No. 1



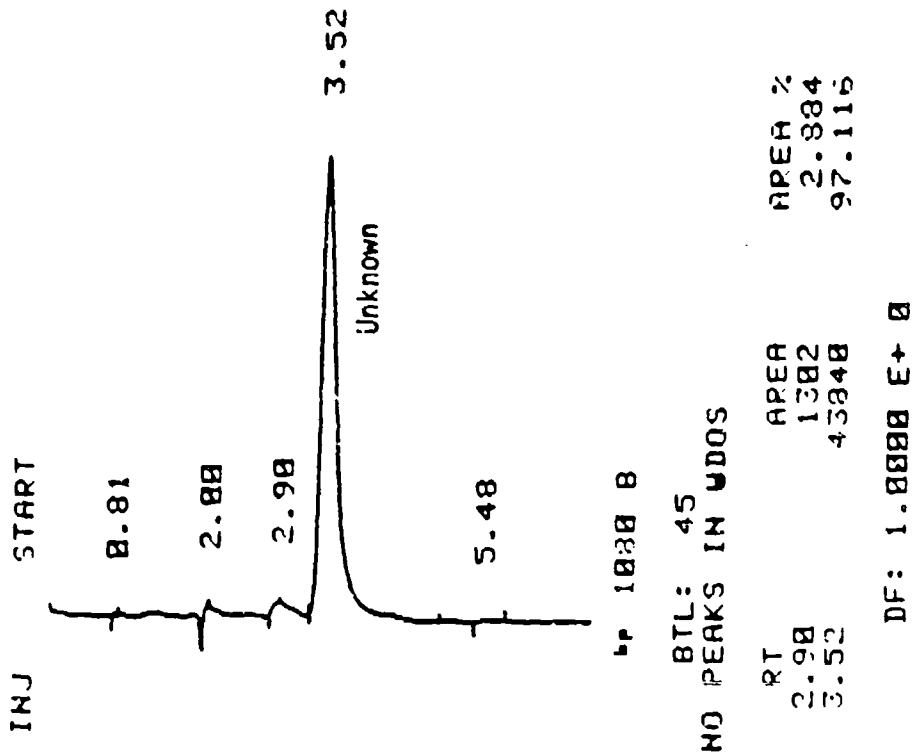


Figure 14. Chromatogram of respirometer sample after 140 h which originally contained 150 mg/L DNT

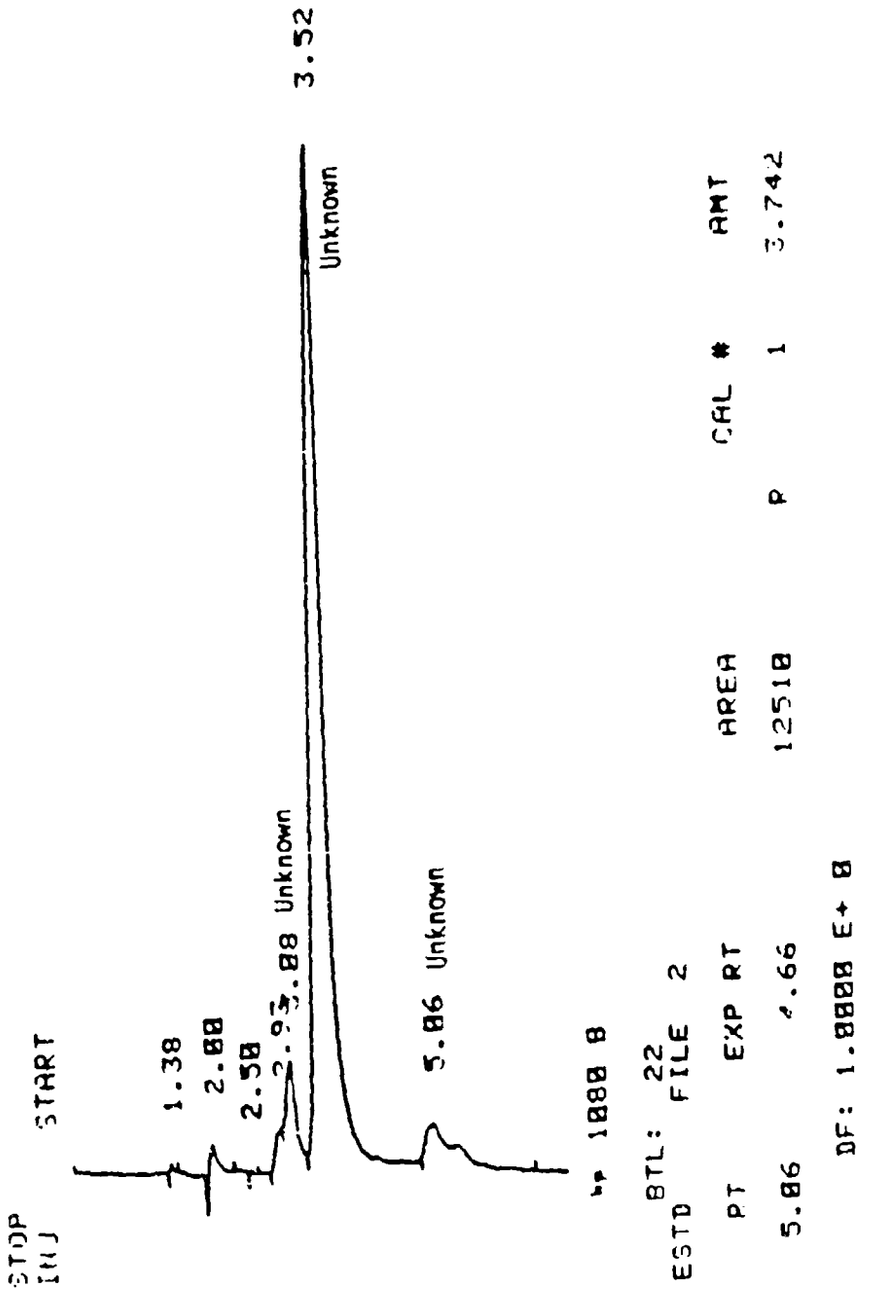


Figure 15. Chromatogram of respirometer sample after 140 h which originally contained 200 mg/L DNT

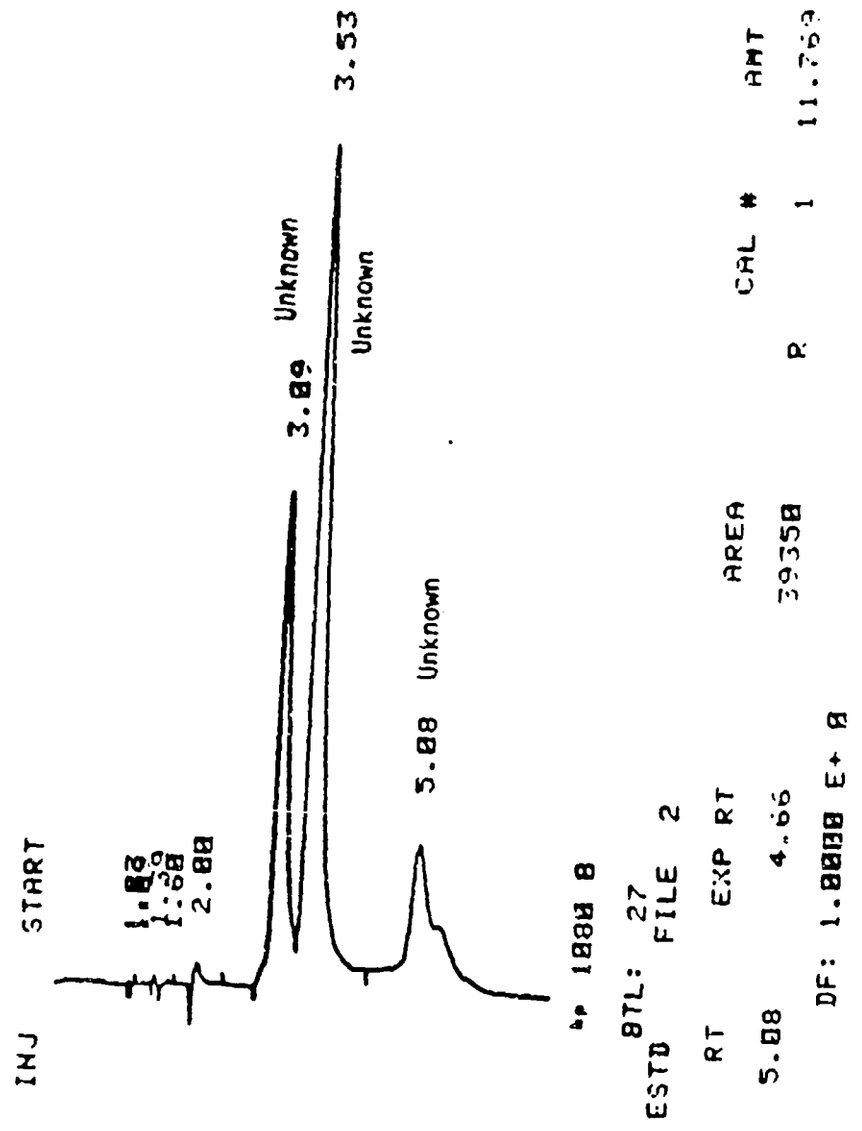


Figure 16. Chromatogram of respirometer sample after 140 h which originally contained 250 mg/L DNT

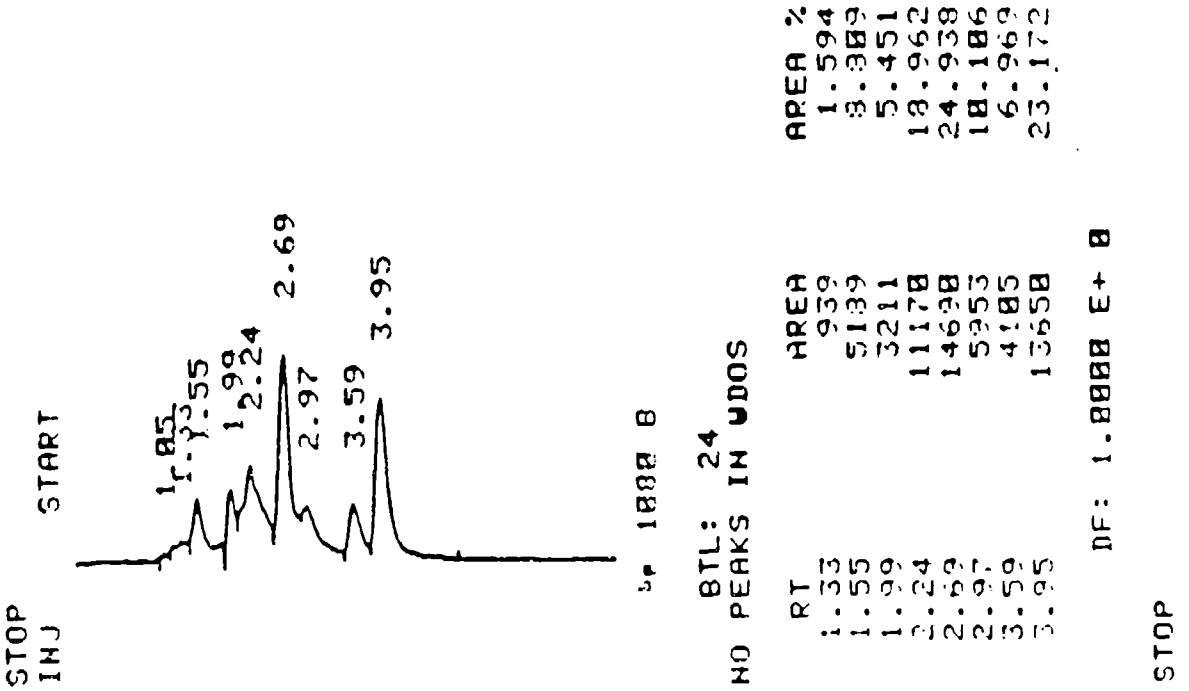


Figure 17. Chromatogram of respirometer sample originally containing 100% seed

Figure 18

RESPIROMETER TOXICITY DATA FOR DNT

Test No. 2

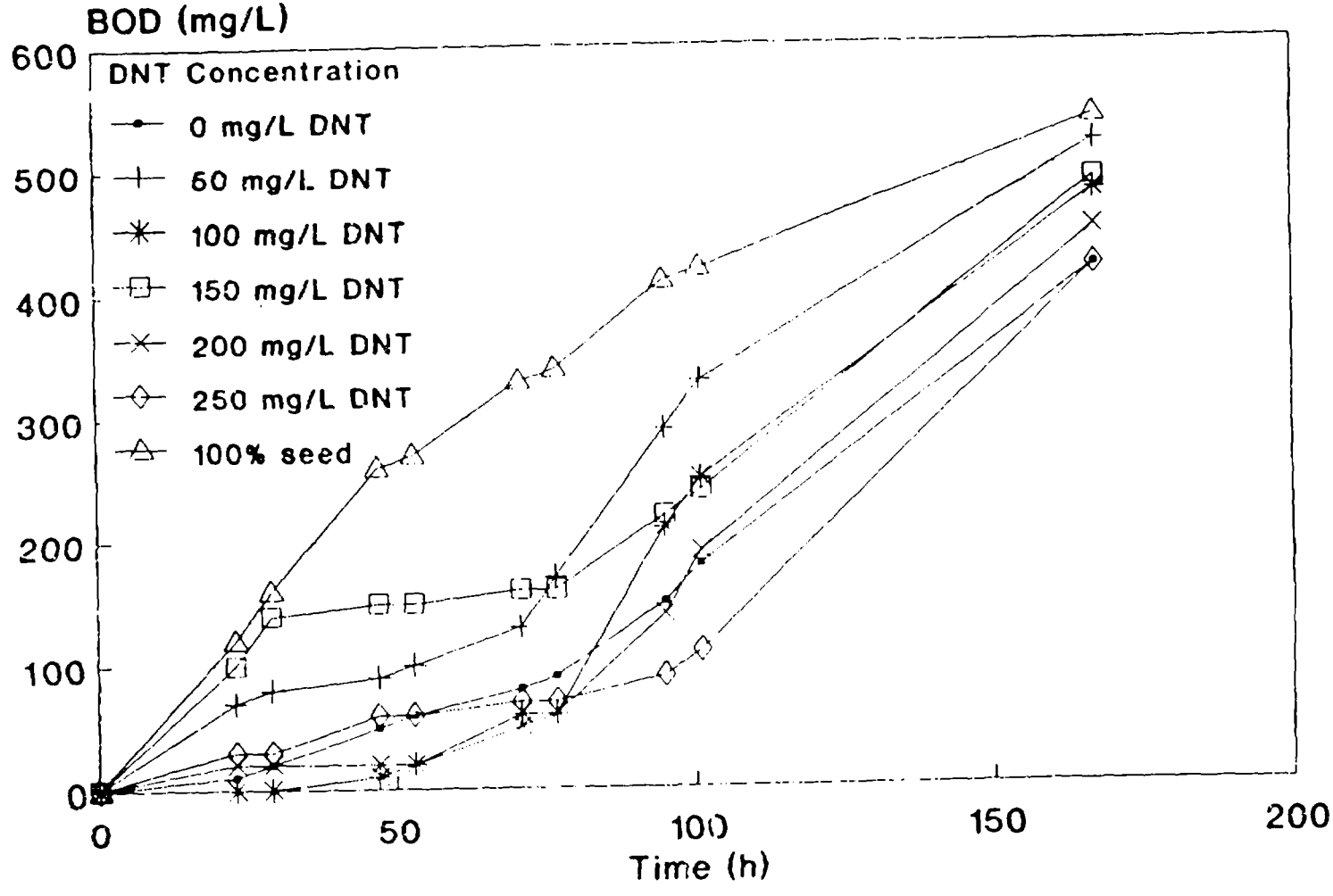


Figure 19

RESPIROMETER TOXICITY DATA FOR DNT

Test No. 3

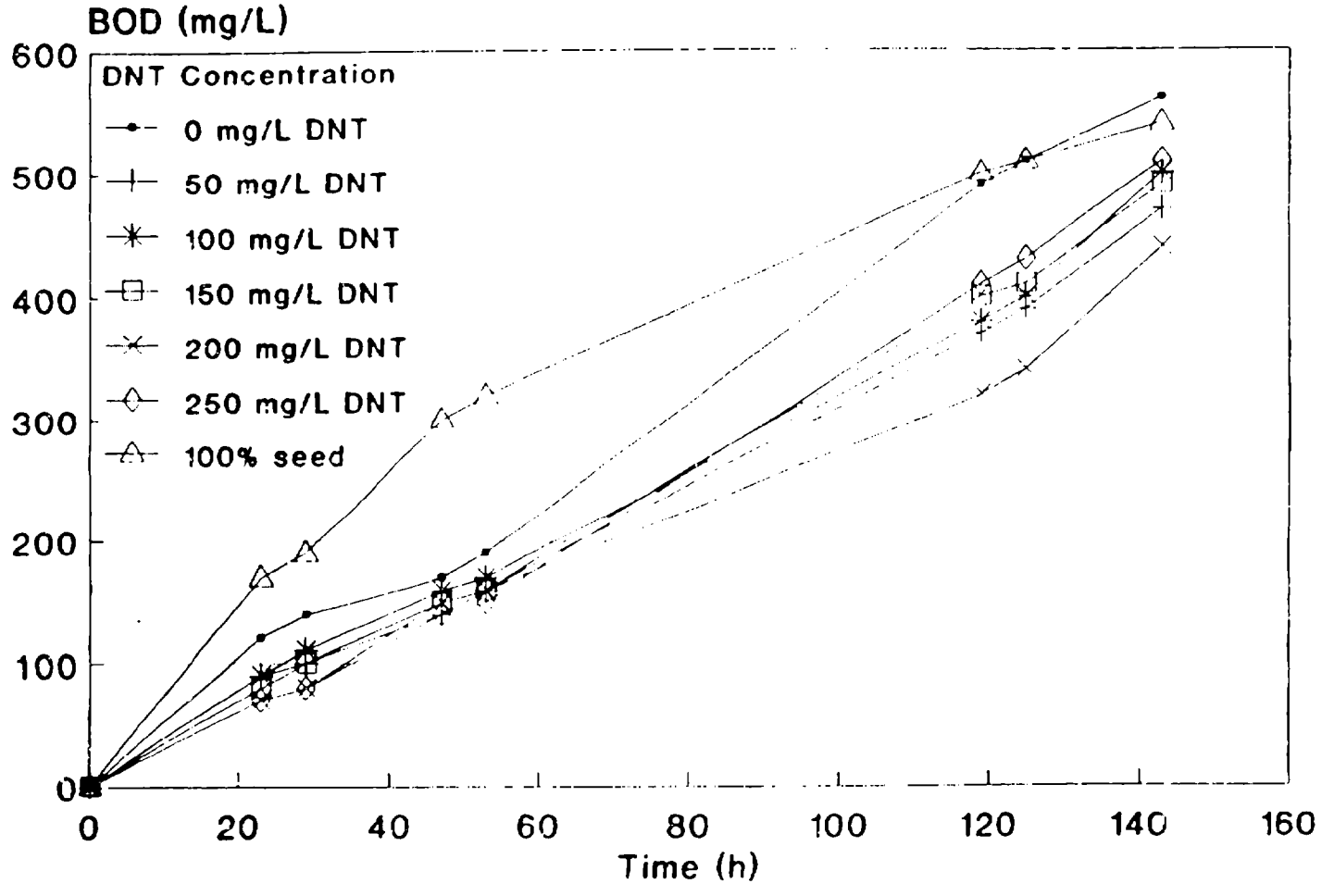


Figure 20

RESPIROMETER TOXICITY DATA FOR DNT

Test No. 4

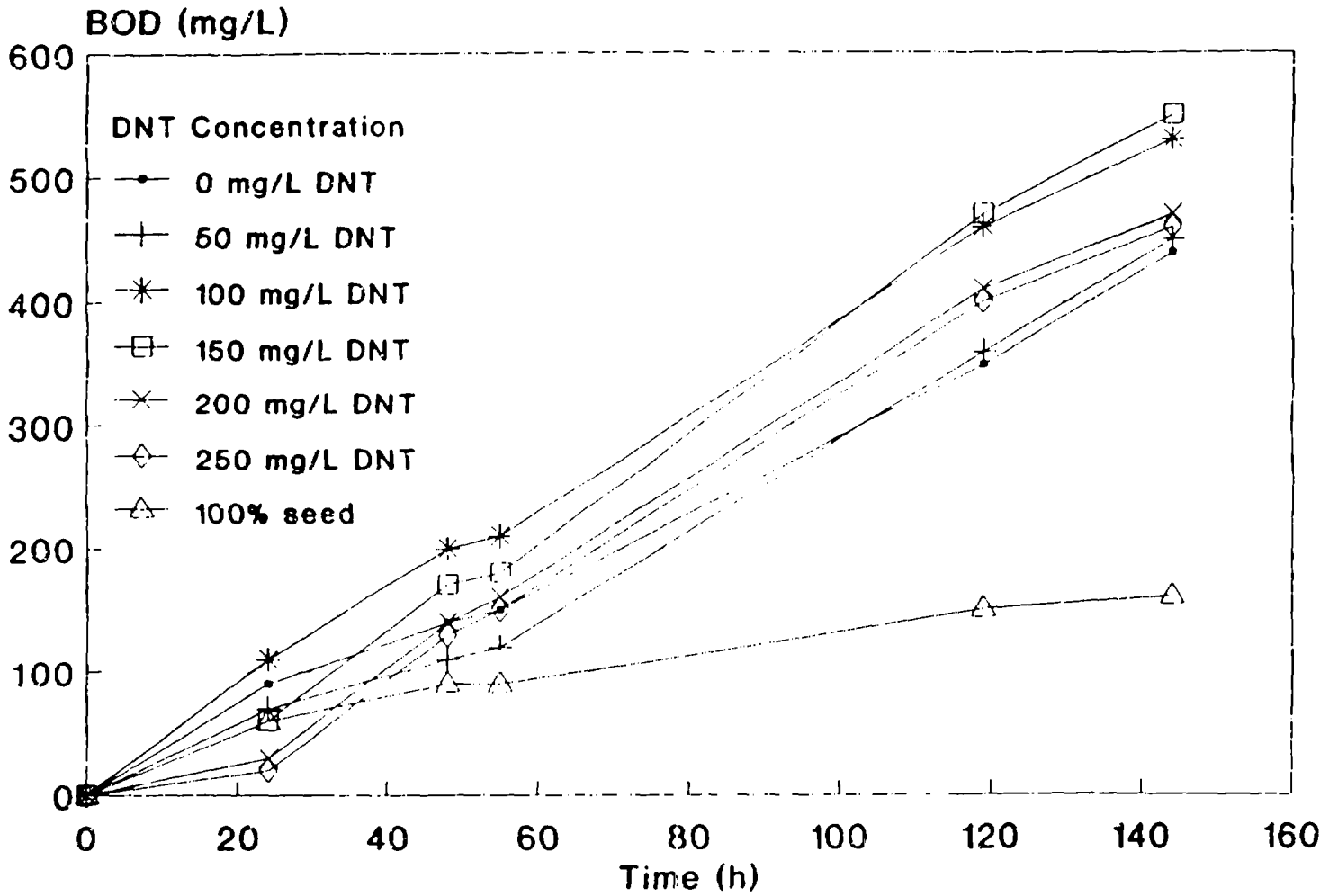


Figure 21

RESPIROMETER TOXICITY DATA FOR DNT

Test No. 5

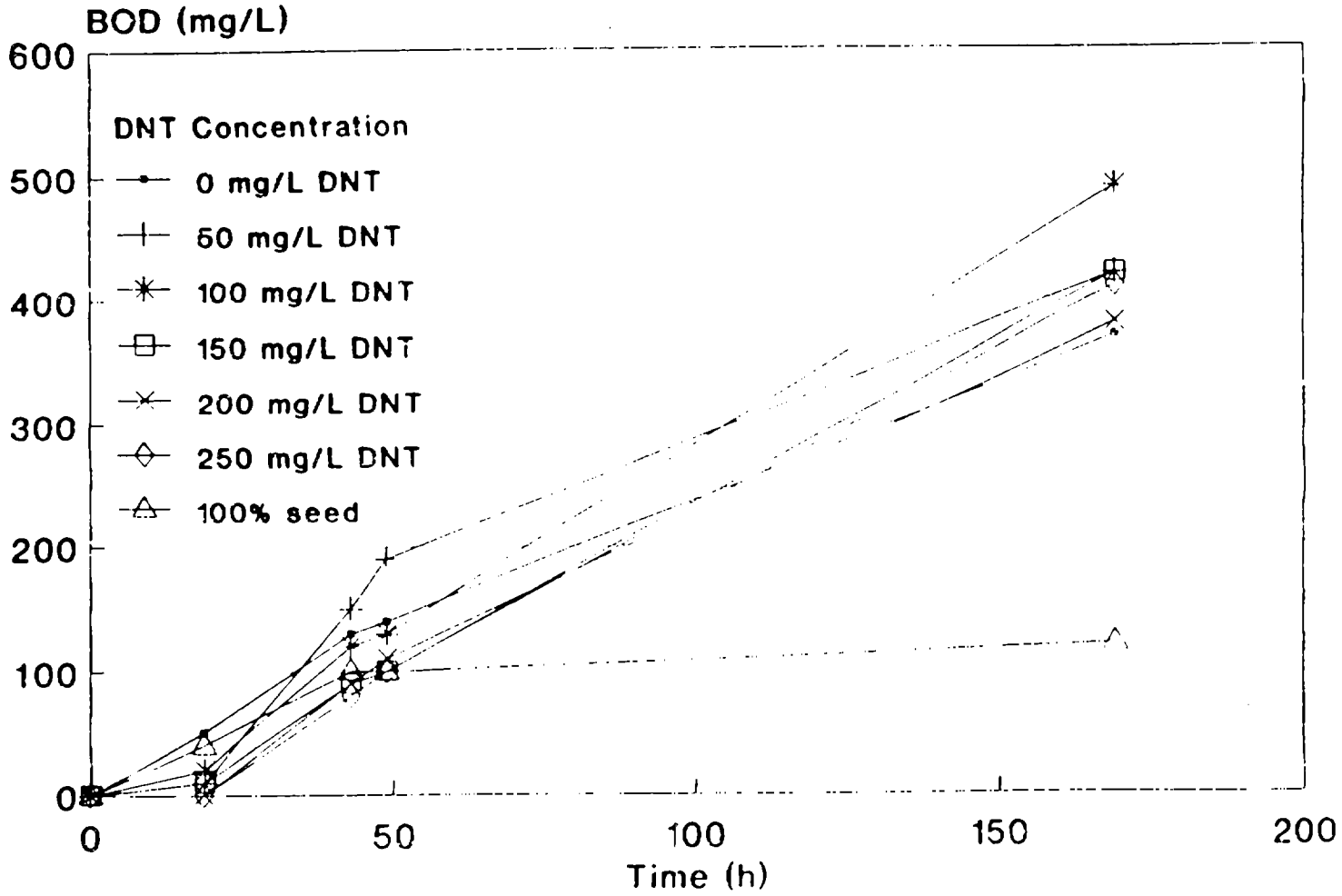


Figure 22. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 0 mg/L

Figure 23. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 50 mg/L

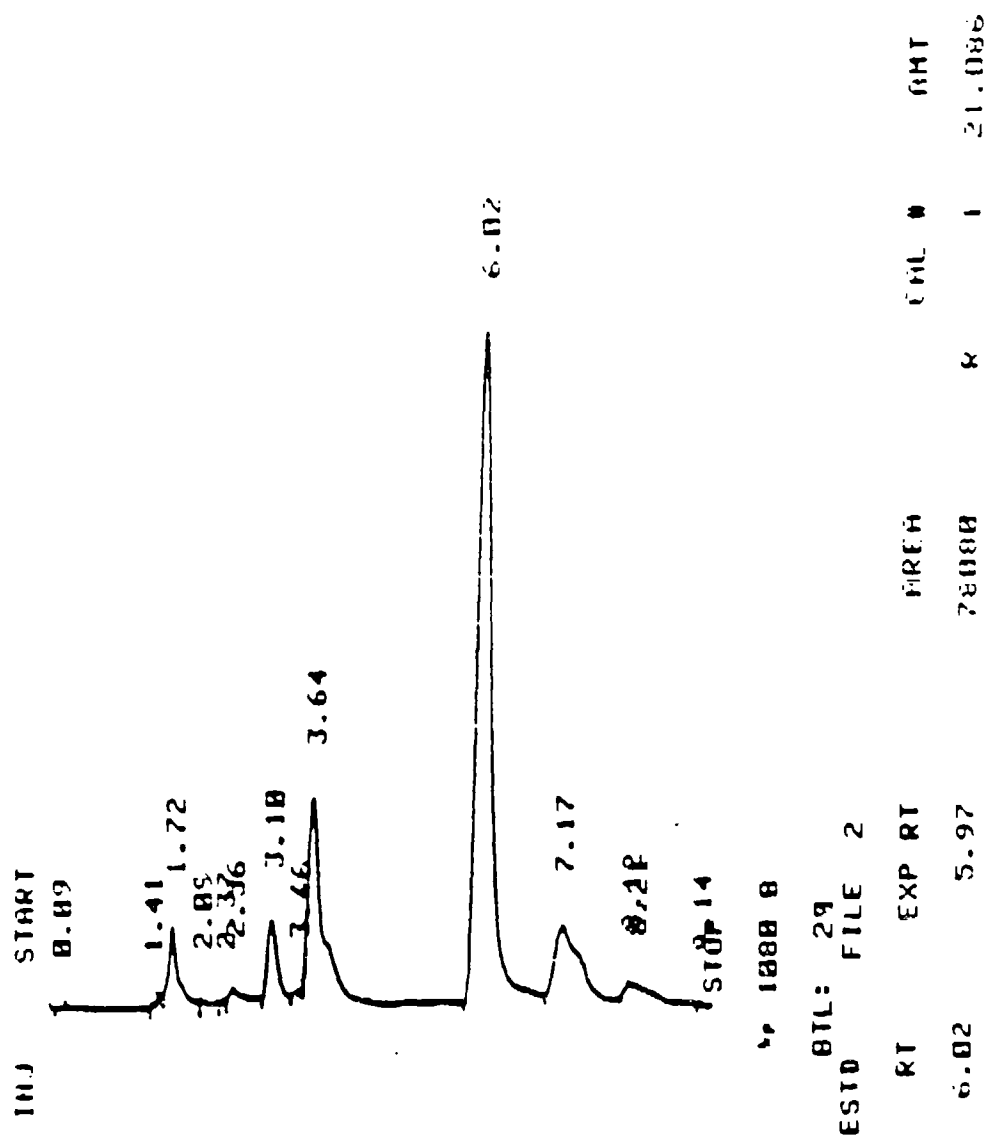


Figure 24. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 100 mg/L

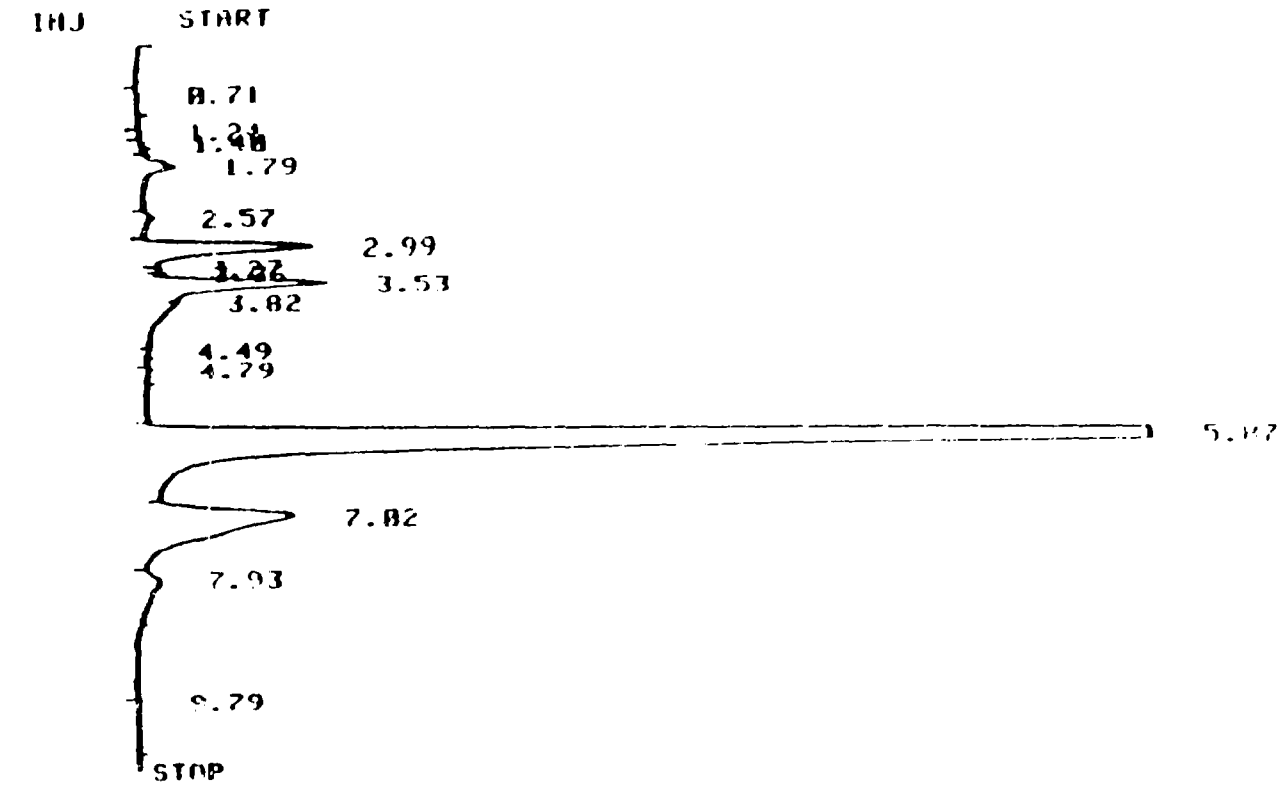


Figure 25. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 150 mg/L

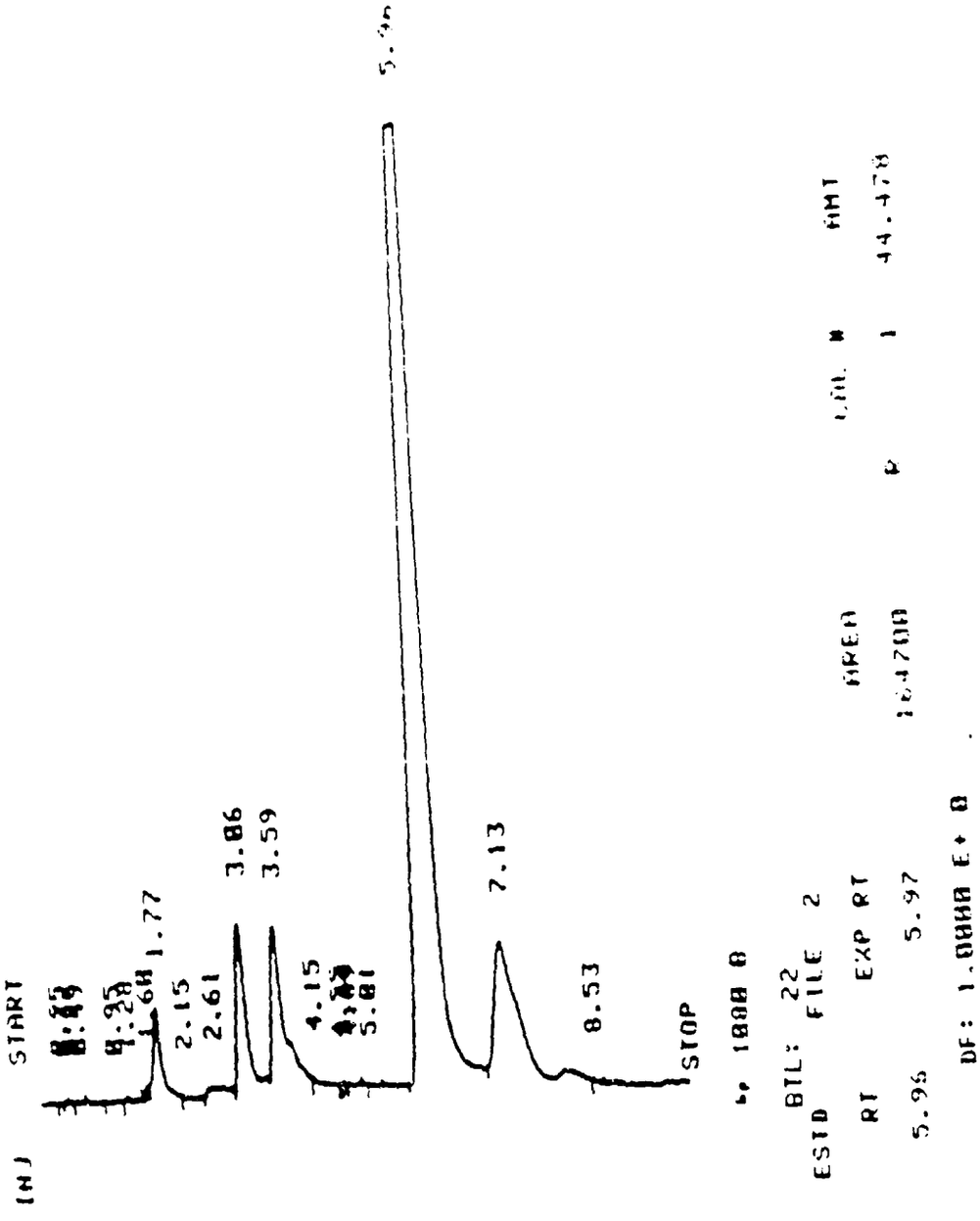


Figure 26. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 200 mg/L

Figure 27. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 250 mg/L

Figure 28. Chromatogram of respirometer toxicity test No. 5 with initial DNT concentration of 0 mg/L (100% seed)

Figure 29. Blank biomass/bioreactor chromatogram on day 0

Figure 30. DNT supplemented biomass/bioreactor chromatogram on day 0

Figure 31. Blank biomass/bioreactor chromatogram on day 1

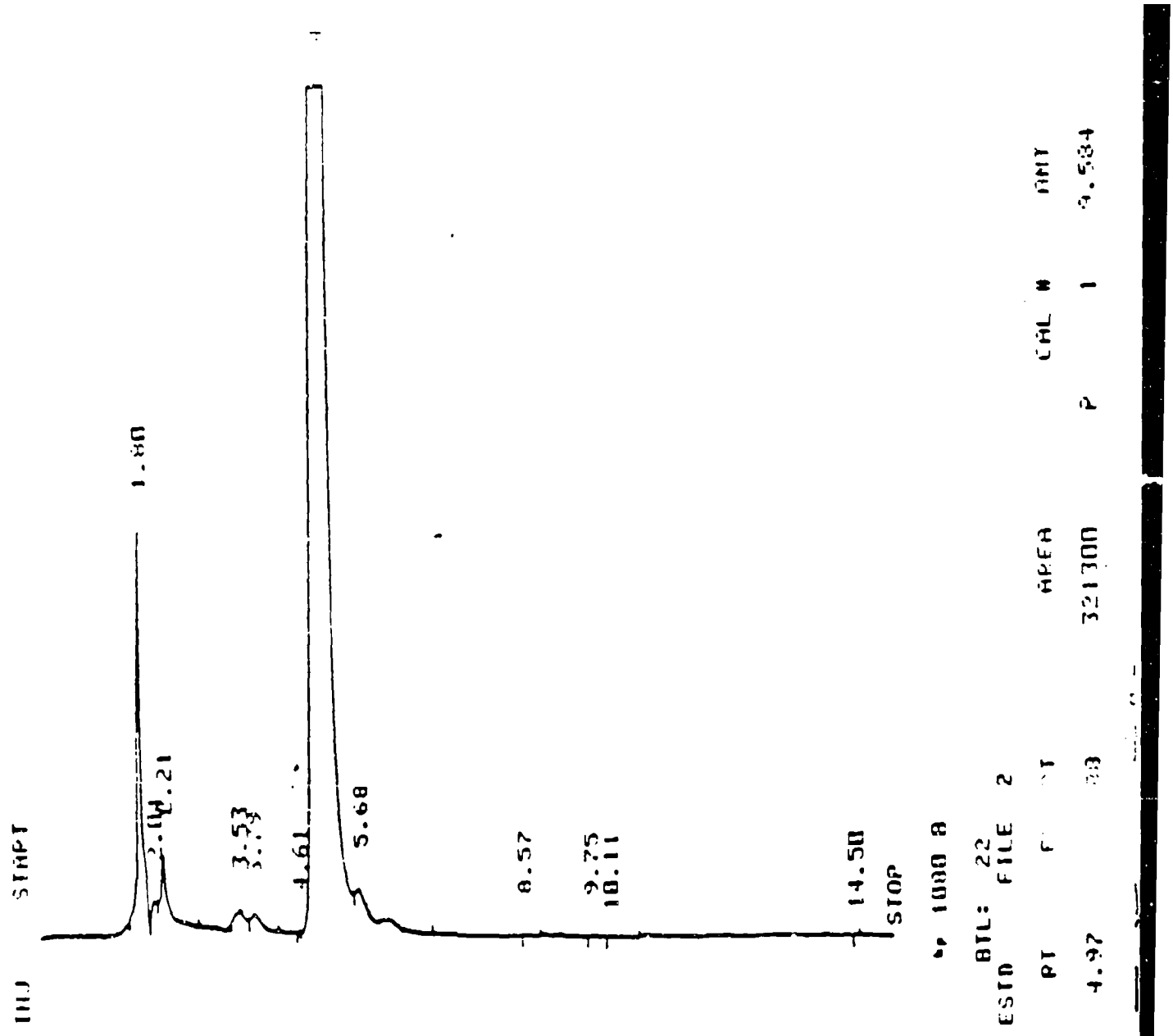


Figure 32. DNT supplemented biomass/bioreactor chromatogram on day 1

Figure 33. Blank biomass/bioreactor chromatogram on day 4

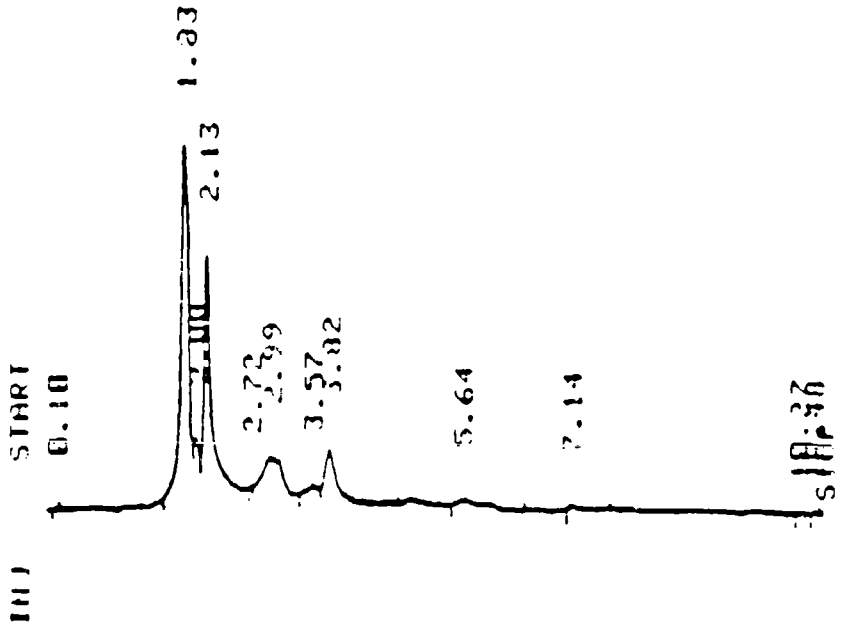


Figure 34. DNT supplemented biomass/bioreactor chromatogram on day 4

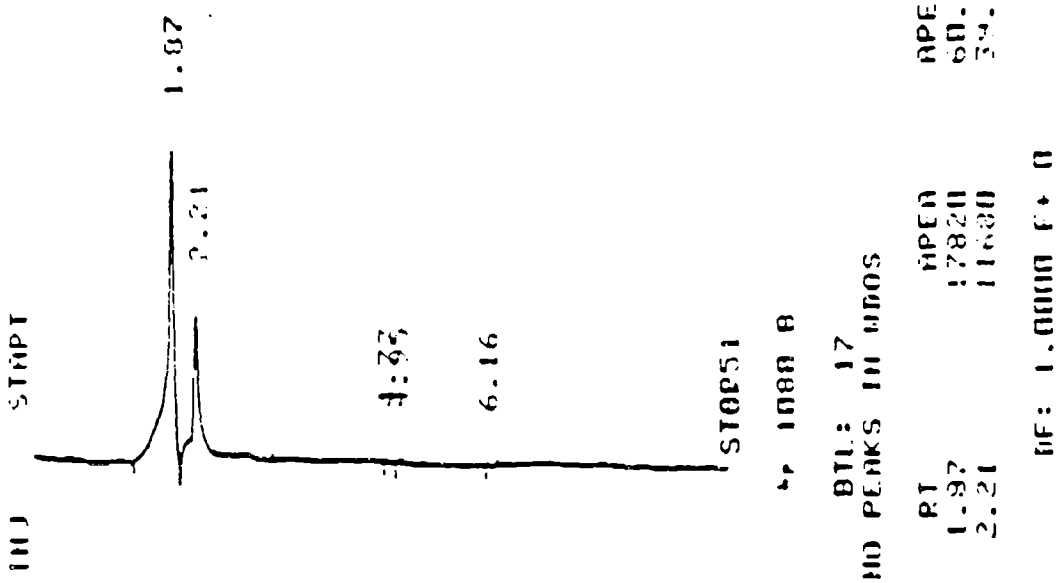


Figure 35. Blank biomass/bioreactor chromatogram on day 6

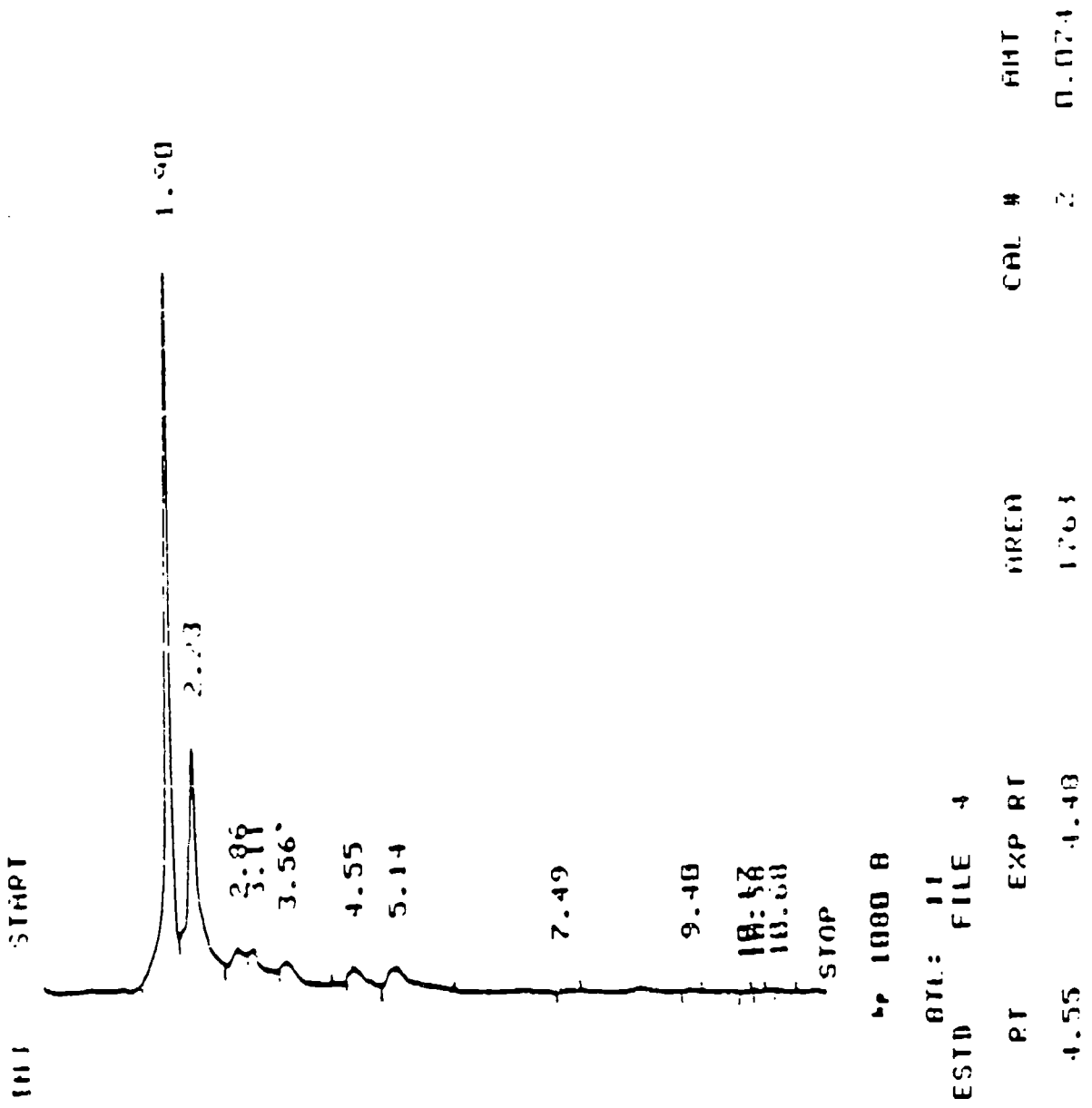


Figure 36. DNT supplemented biomass/bioreactor chromatogram on day 6

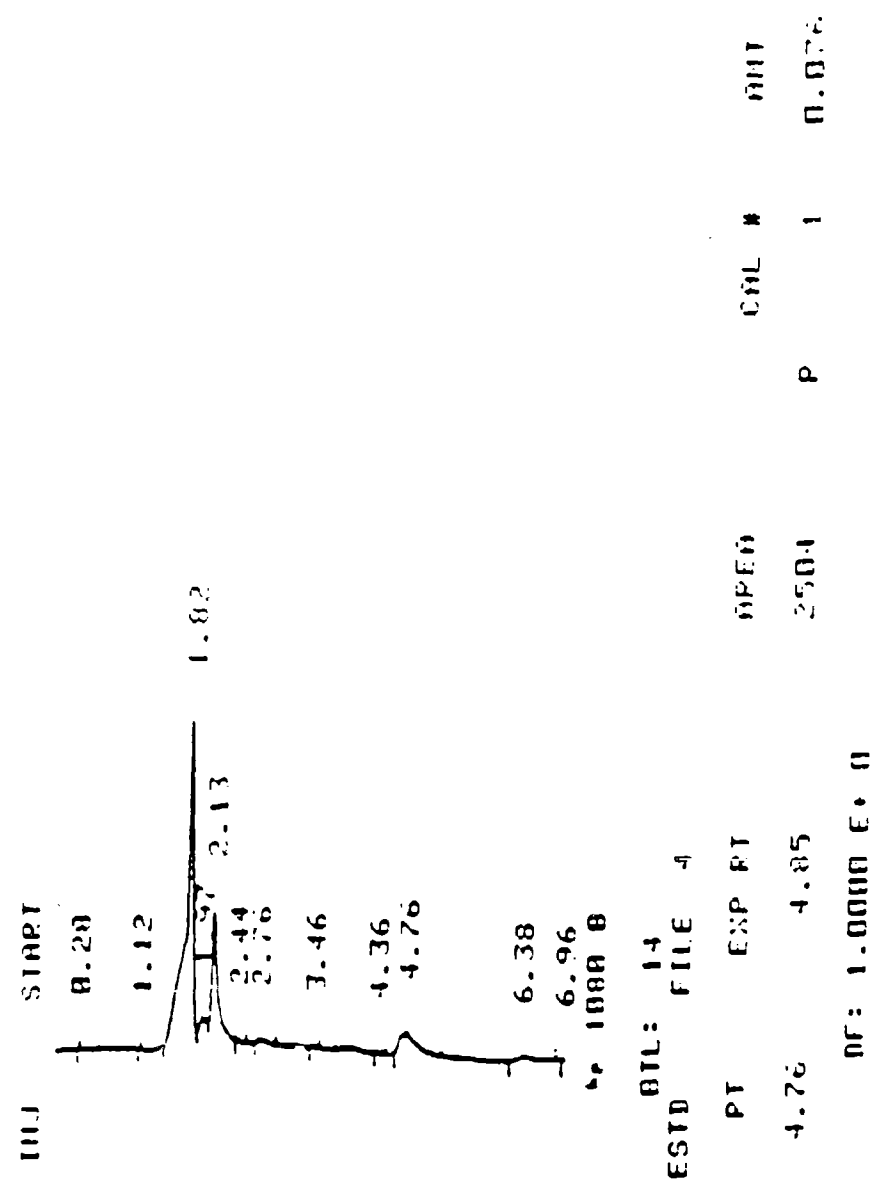


Figure 37. Blank biomass/bioreactor chromatogram on day 7

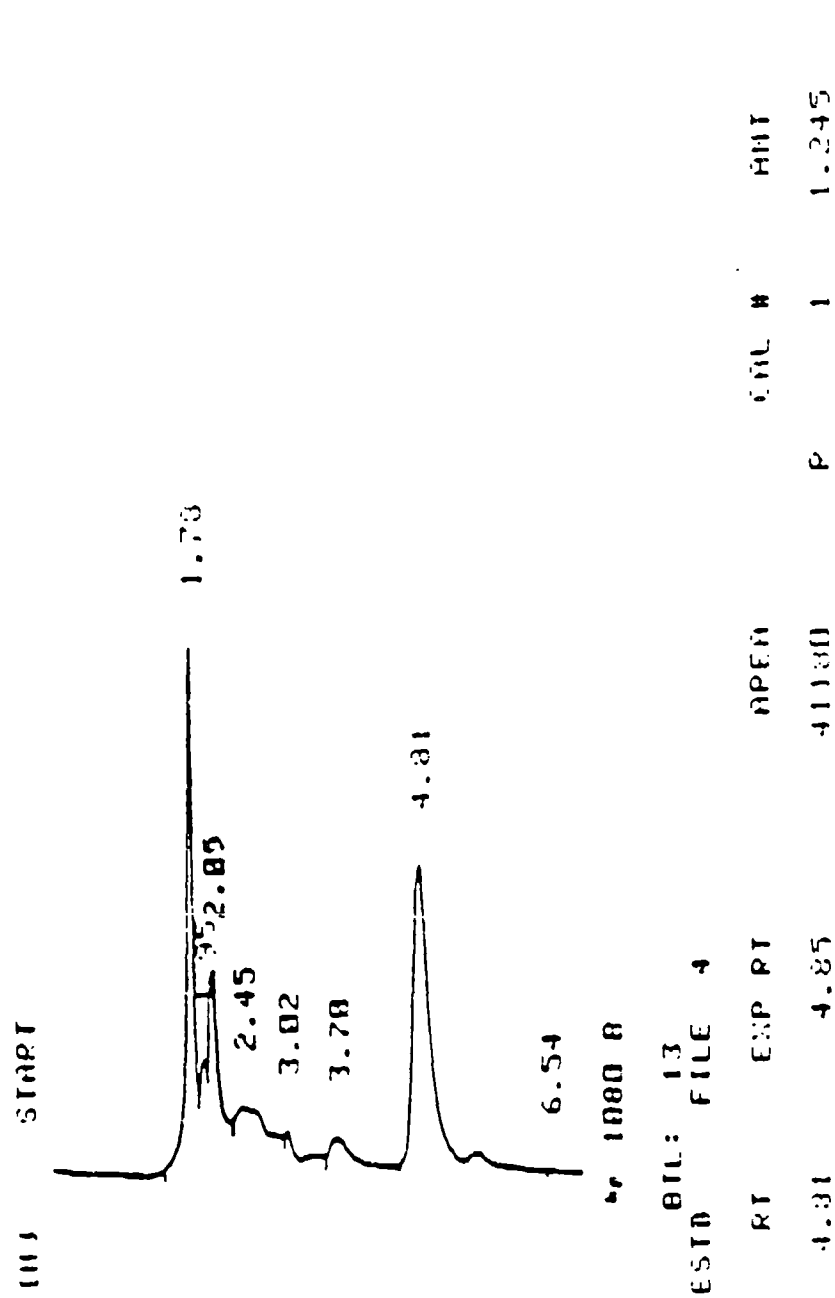


Figure 38. DNT supplemented biomass/bioreactor chromatogram on day 7

Figure 39. Blank biomass/bioreactor chromatogram on day 8

Figure 40. DNT supplemented biomass/bioreactor chromatogram on day 8

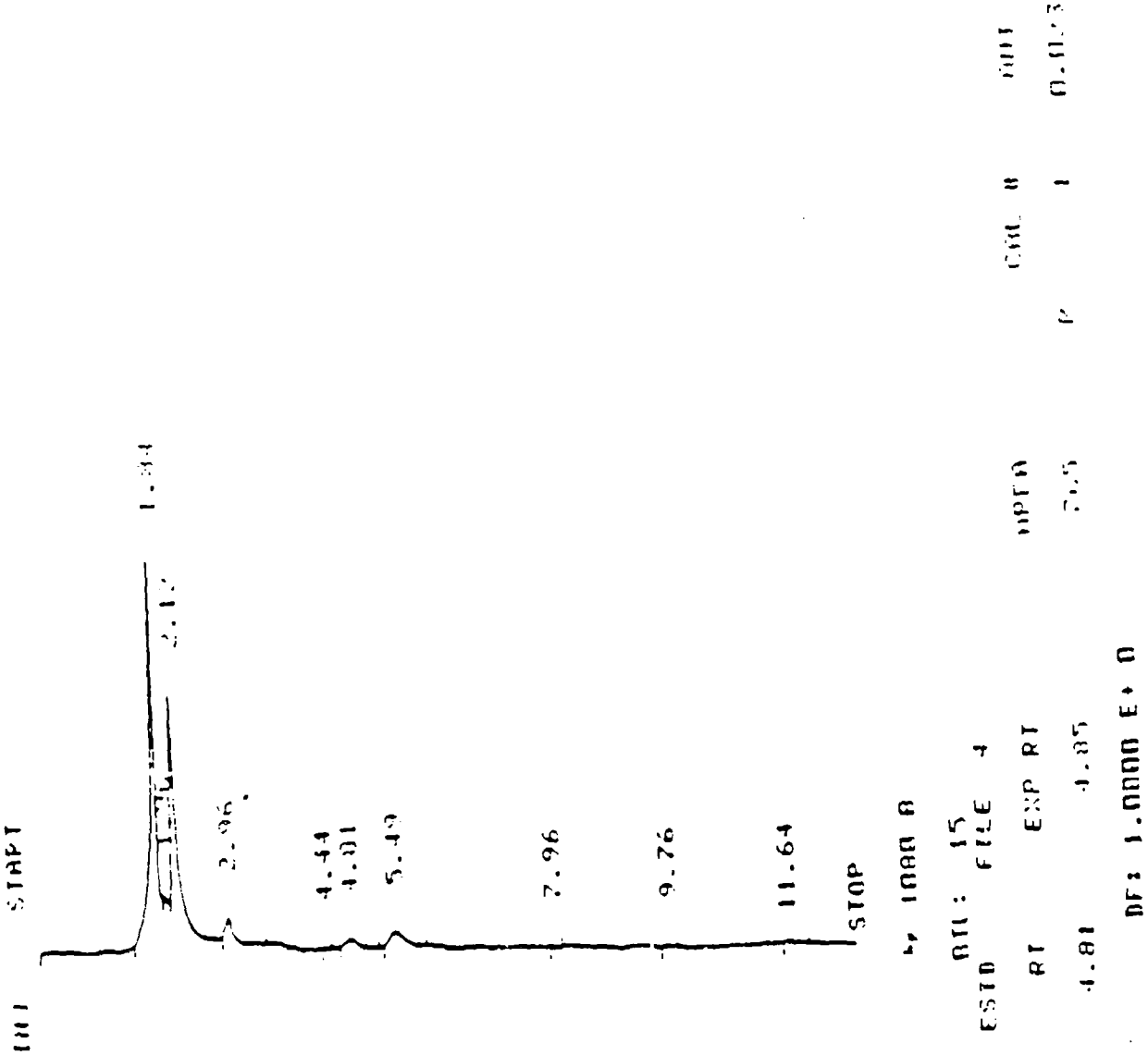


Figure 41. Blank biomass/bioreactor chromatogram on day 11

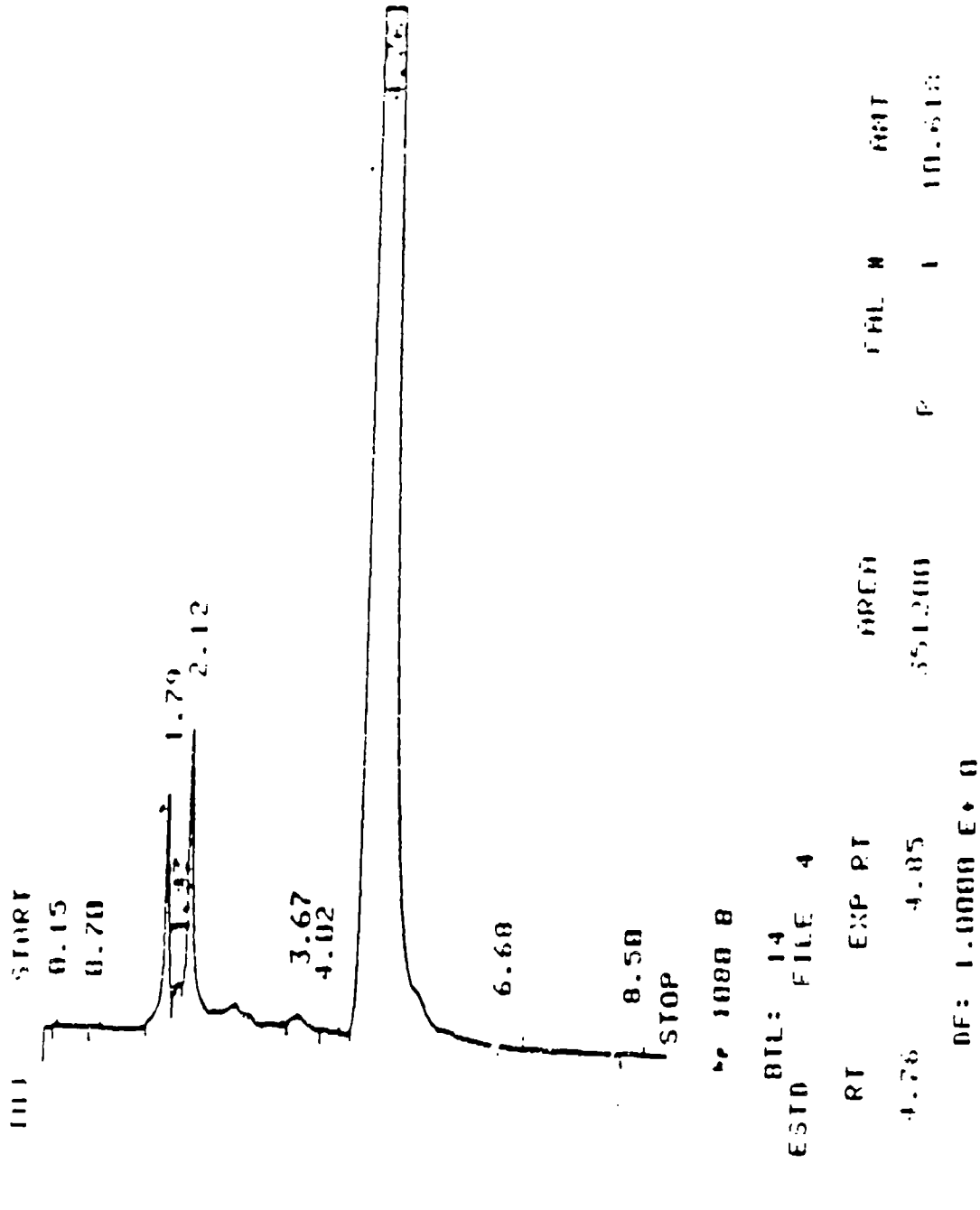


Figure 42. DHT supplemented biomass/bioreactor chromatogram on day 11

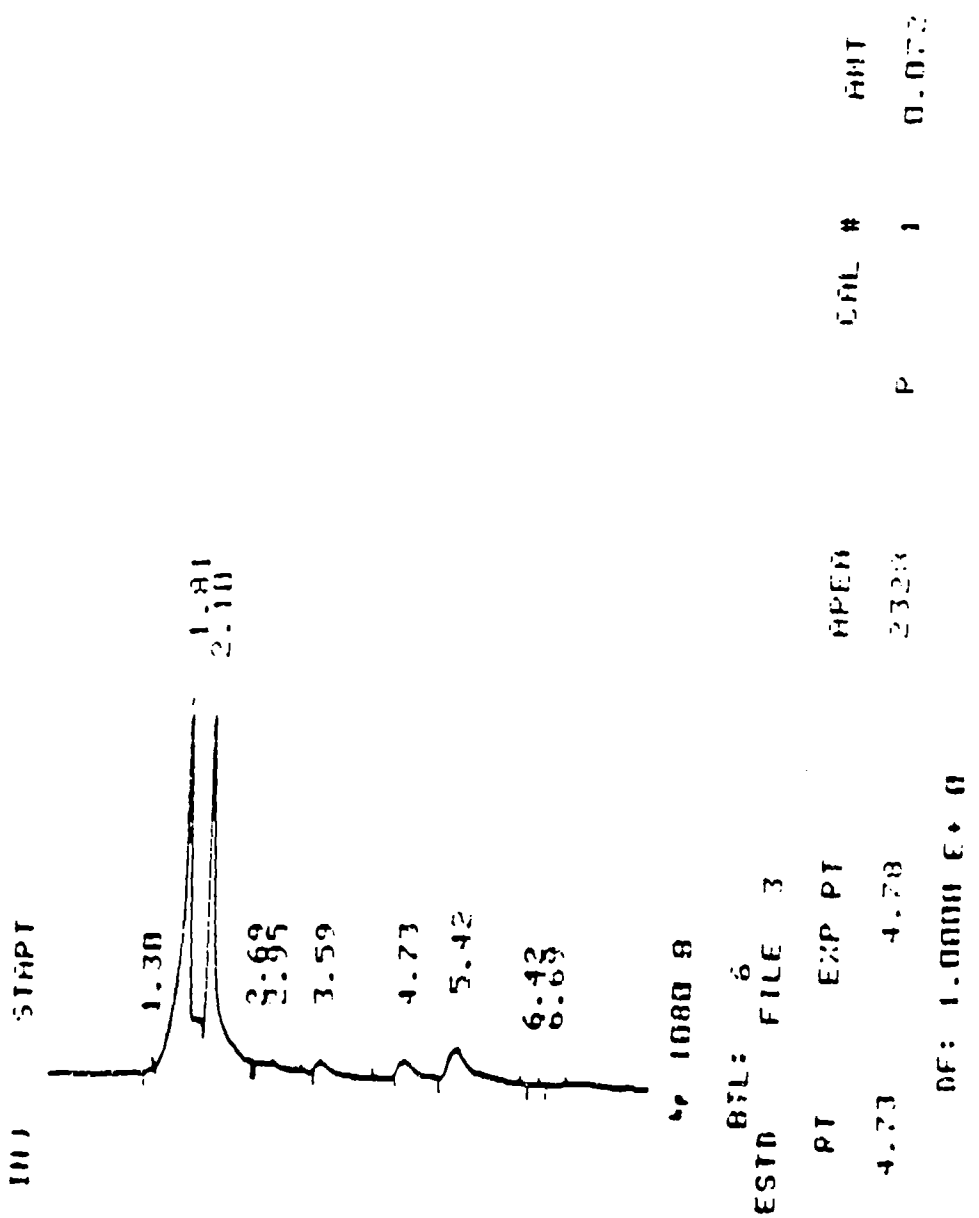


Figure 43. Blank biomass/bioreactor chromatogram on day 12

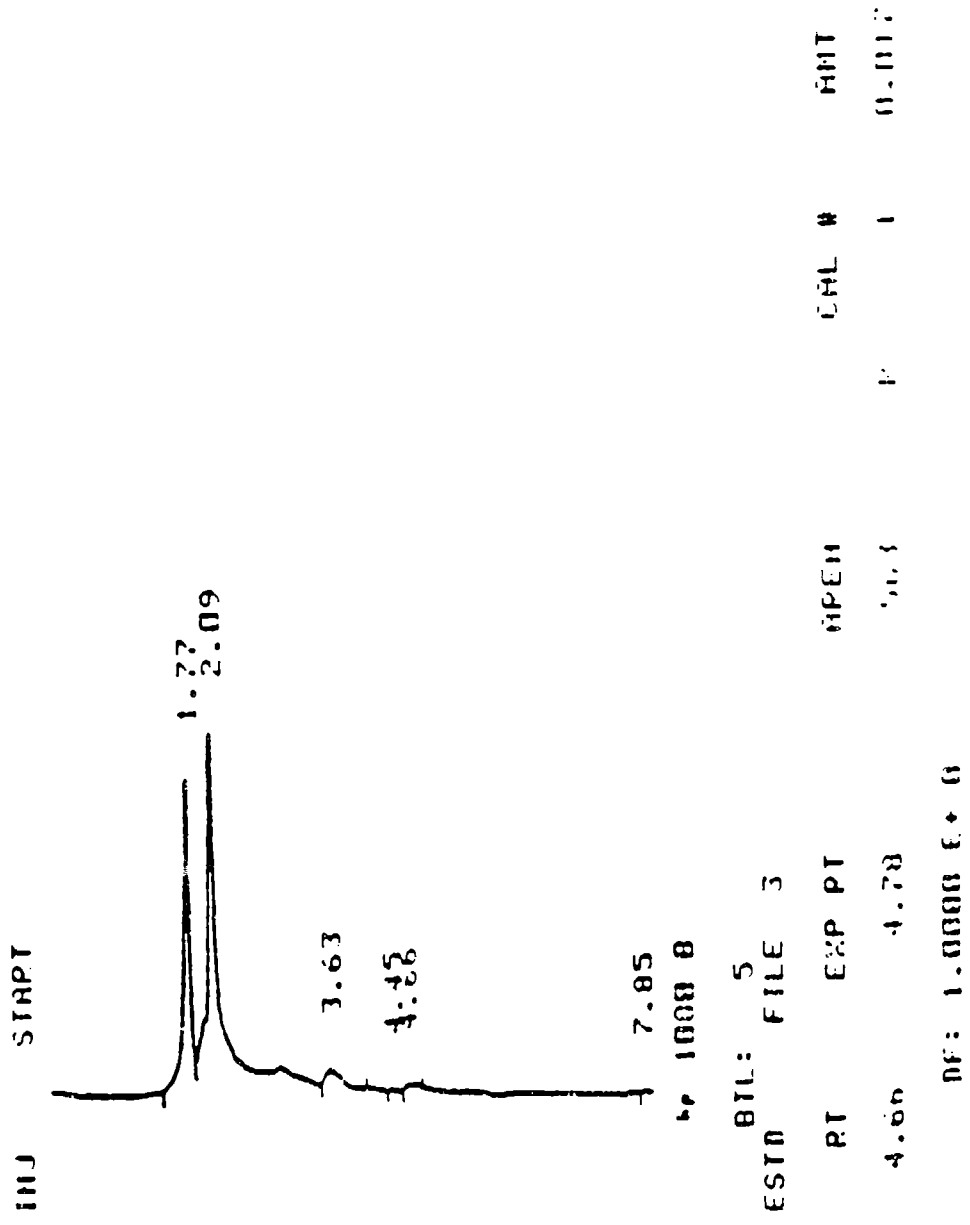
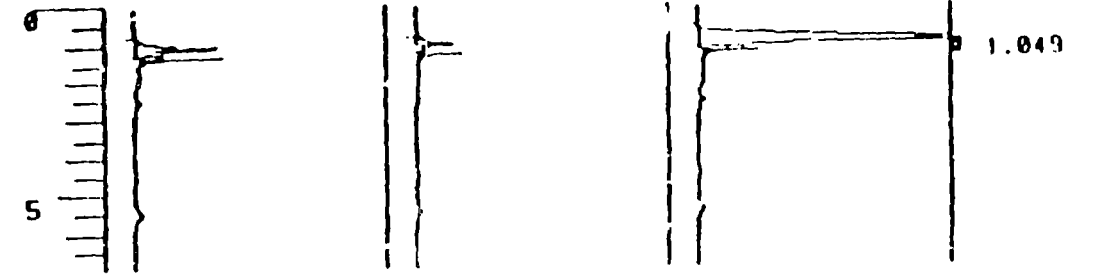


Figure 44. DNT supplemented biomass/bioreactor chromatogram on day 12

Integration of new analysis
VIAL 8 INJ 1

Offline plot from CPU memory

Signal	A	B	C	Annotation
S wl,bw	254,20	280,20	260,80	
Range	100	100	100	
Zero %	10	10	10	



NO CALIBRATED PEAKS FOUND

AREA%

#	SI	TIME [min]	AREA [mAUs]	TYPE	AREA%	HEIGHT [mAU]	WIDTH [min]	dTIME [min]		QUOTIENT [area]
	C	1.049	1399.1	BP	97.332	122.80	0.154			
	A	1.059	203.97	BP	77.851	29.155	0.092			
	B	1.065	70.777	BV	67.820	13.791	0.069			
	A	1.302	58.030	PB	22.149	31.171	0.028	0.000	A/B	1.720

TOTAL AREA FOR SIGNAL A = 262
TOTAL AREA FOR SIGNAL B = 104
TOTAL AREA FOR SIGNAL C = 1437

MUL FACTOR = 1

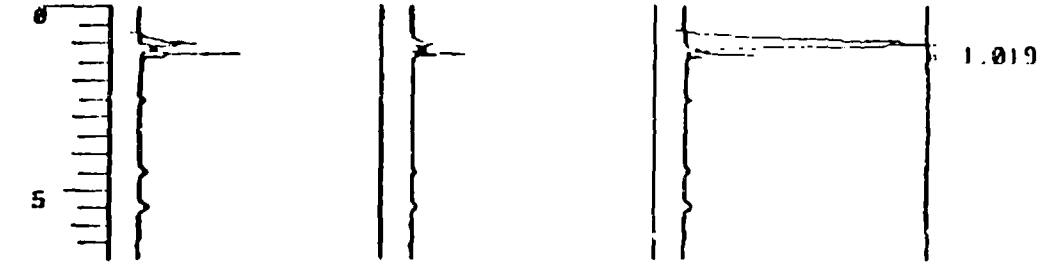
Figure 45. Blank biomass/bioreactor chromatogram on day 13

Figure 46. DNT supplemented biomass/bioreactor chromatogram on day 13

Integration of new analysis
VIAL 3 INJ 1

Offline plot from CPU memory

Signal	A	B	C	Annotation
S wl,bw	254,20	280,20	260,80	
Range	100	100	100	
Zero %	10	10	10	



NO CALIBRATED PEAKS FOUND

AREA%

B	SI	TIME (min)	AREA (mAUs)	TYPE	AREA%	HEIGHT (mAU)	WIDTH (min)	dTIME (min)		QUOTIENT (area)
	C	1.019	1308.9	BV	94.920	100.41	0.150			
	A	1.027	151.71	BV	60.900	19.851	0.102			
	A	1.299	97.400	VB	39.100	37.059	0.038	0.000	A/B	2.610

TOTAL AREA FOR SIGNAL A = 249
TOTAL AREA FOR SIGNAL B = 37
TOTAL AREA FOR SIGNAL C = 1379

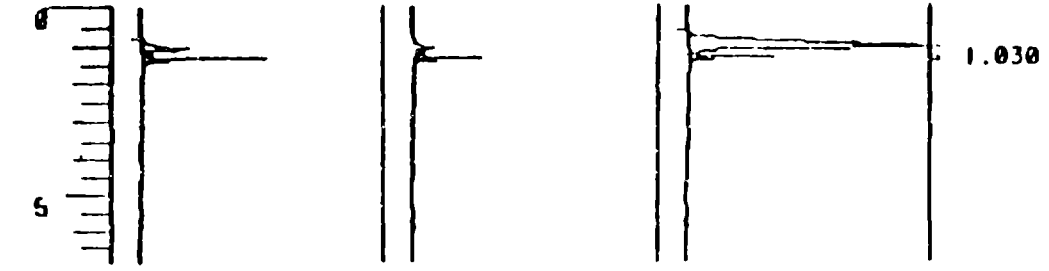
MUL FACTOR = 1

Figure 47. DNT supplemented biomass/bioreactor chromatogram on day 14

Integration of new analysis
VIAL 2 INJ 1

Offline plot from DPU memory

Signal	A	B	C	Annotation
S wl,bw	254,20	280,20	260,80	
Range	100	100	100	
Zero %	10	10	10	



NO CALIBRATED PEAKS FOUND

AREA%

#	SI	TIME [min]	AREA [mAUs]	TYPE	AREA%	HEIGHT [mAU]	WIDTH [min]	dTIME [min]		QUOTIENT [area]
	C	1.030	986.00	BV	93.623	89.567	0.149			
	A	1.042	110.06	BV	48.939	17.576	0.002			
	A	1.301	114.83	VB	51.061	46.519	0.035	0.000	A/B	2.365

TOTAL AREA FOR SIGNAL A = 225
TOTAL AREA FOR SIGNAL B = 49
TOTAL AREA FOR SIGNAL C = 1053

MUL FACTOR = 1

Figure 48. ONT supplemented biomass/bioreactor chromatogram on day 14

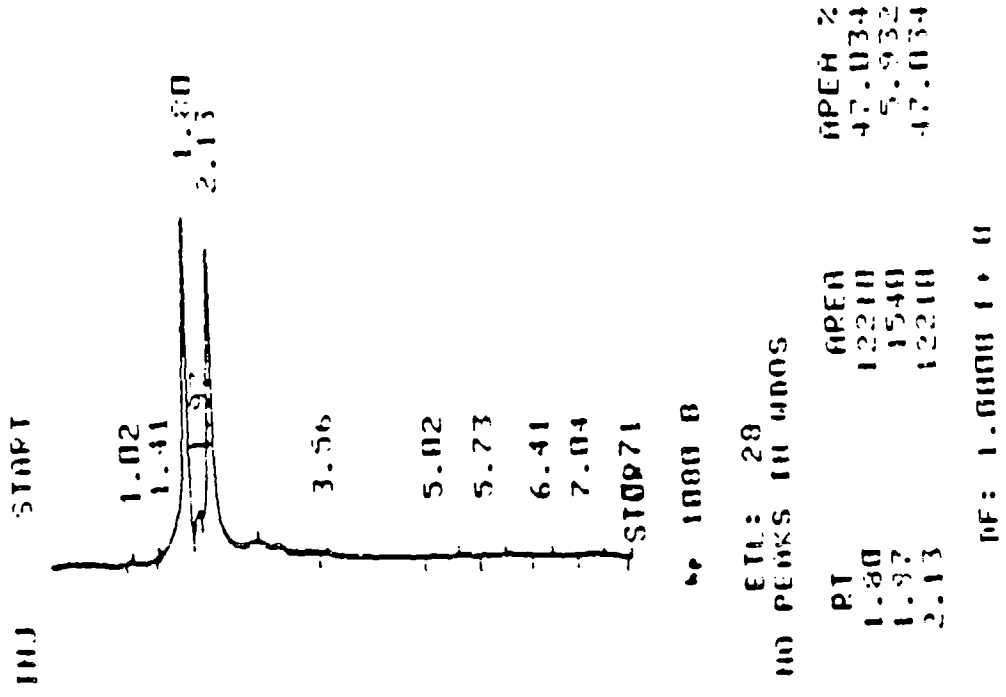


Figure 49. Blank biomass/bioreactor chromatogram on day 15

Figure 50. DNT supplemented biomass/bioreactor chromatogram on day 15

Figure 51. Biodegradation chromatogram of seed at 0 h

Figure 52. Biodegradation chromatogram of initial nutrient water at 0 h

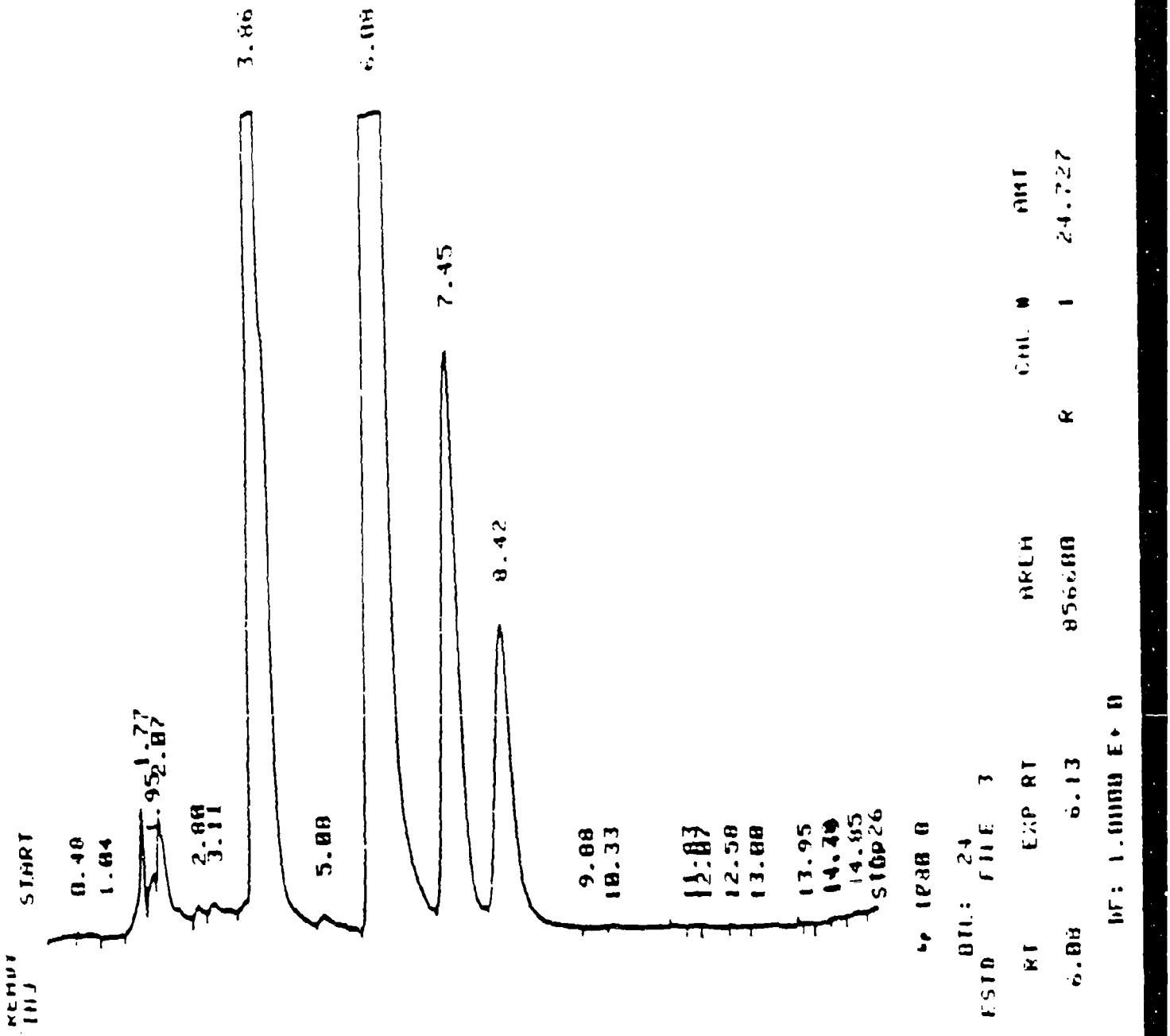


Figure 53. Biodegradation chromatogram of reaction vessel 1 at 23 h

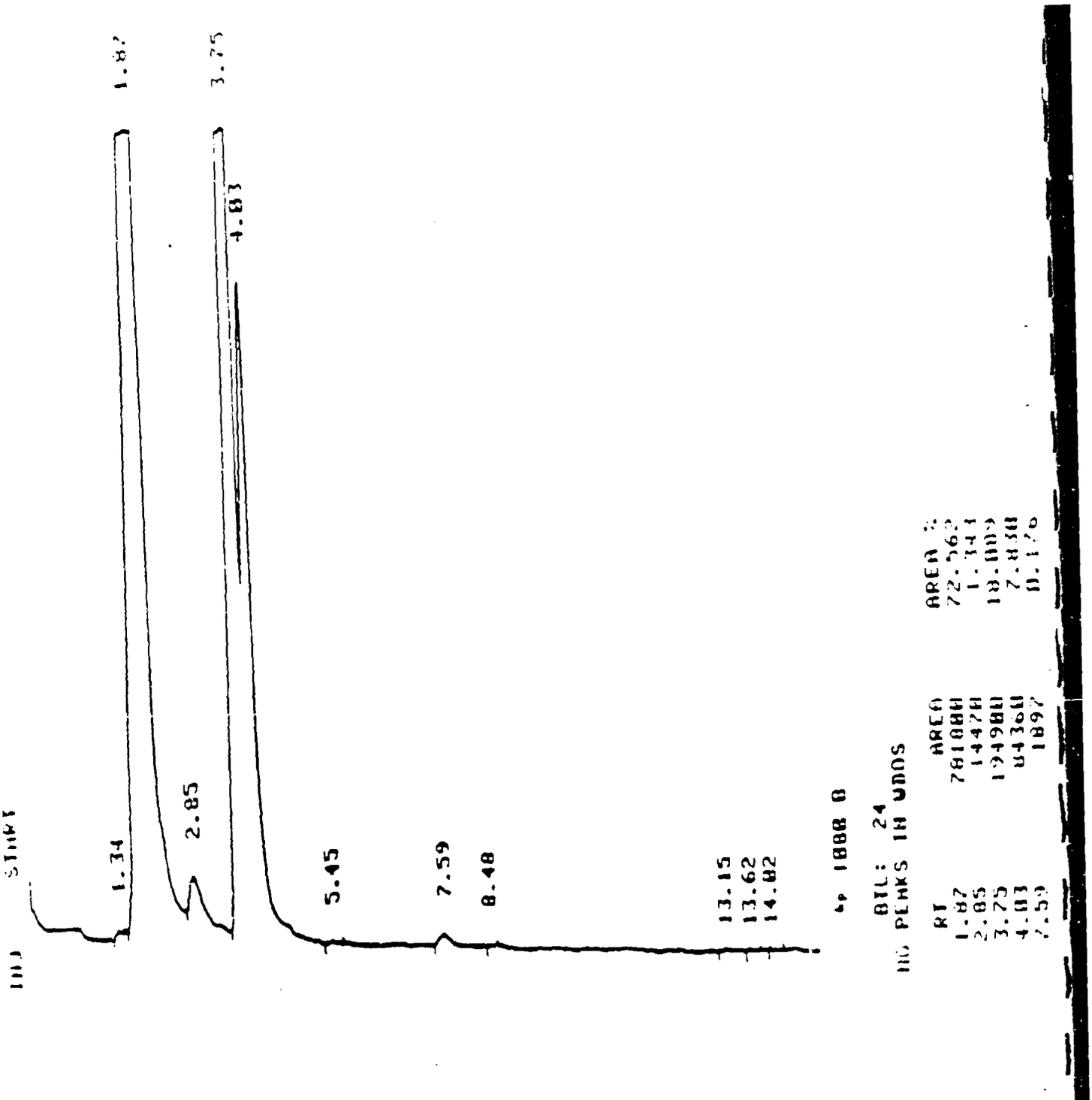


Figure 54. Biodegradation chromatogram of reaction vessel 2 at 77 h

Figure 55. Biodegradation chromatogram of reaction vessel 3 at 95 h

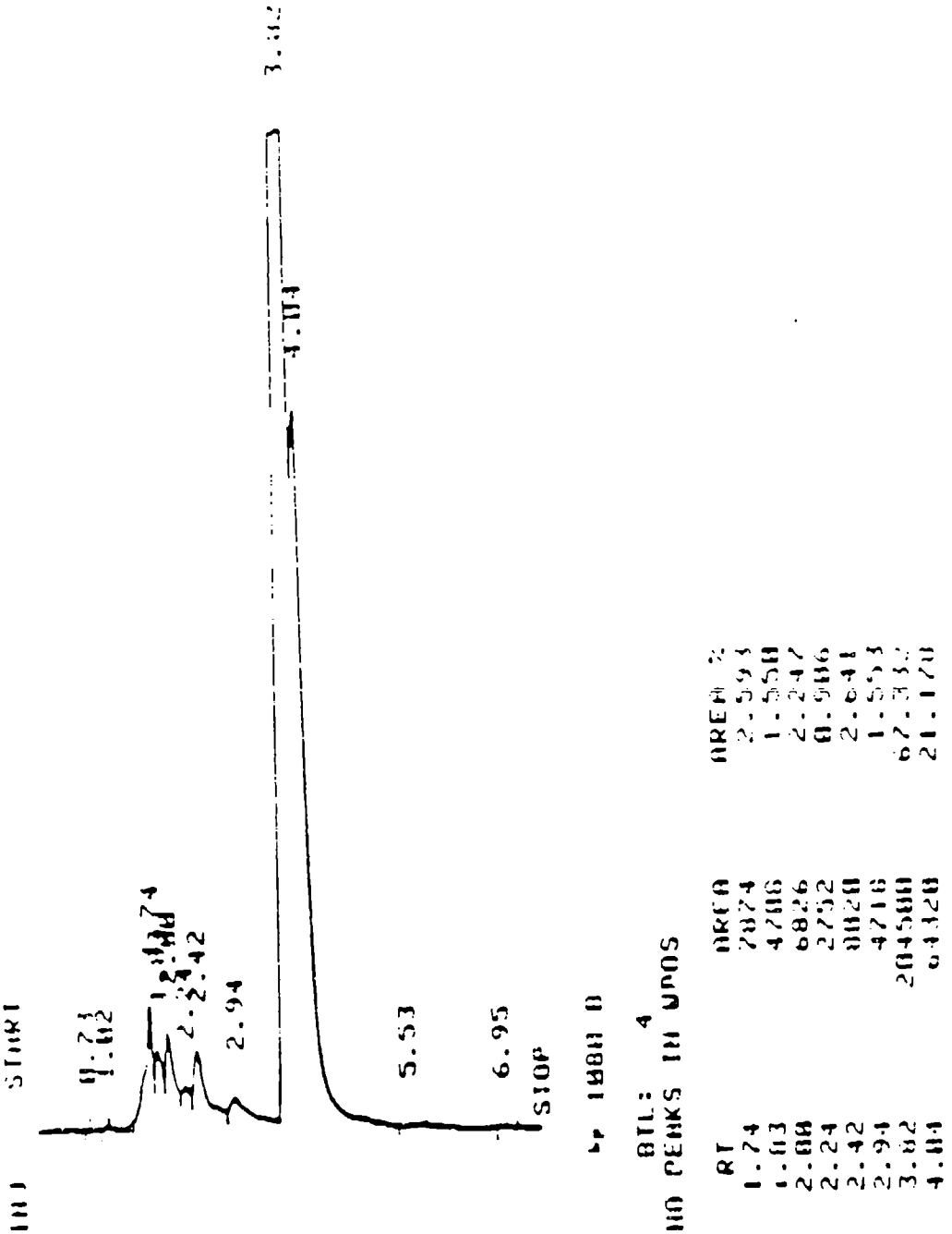


Figure 56. Biodegradation chromatogram of reaction vessel 4 at 119 h

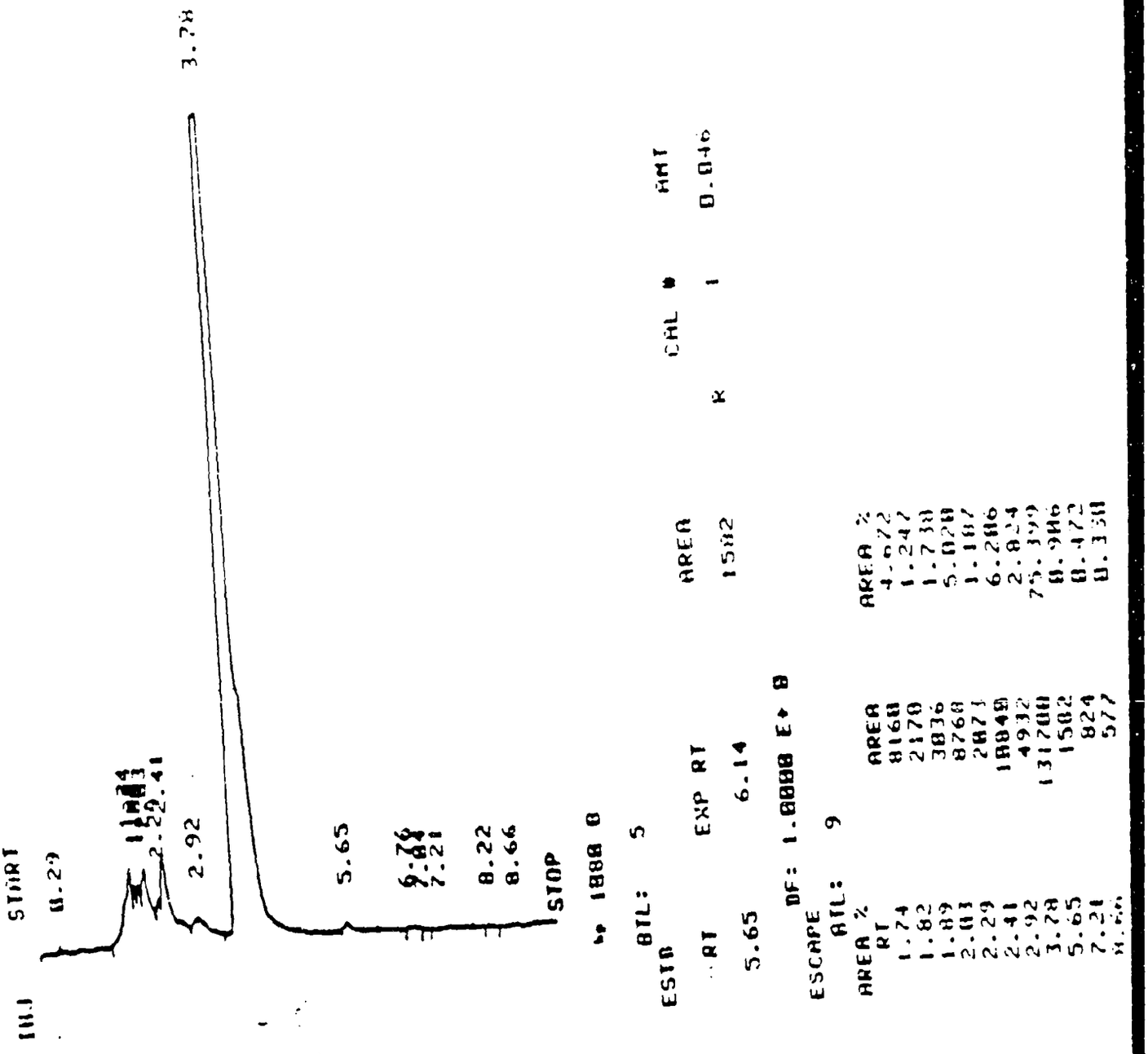


Figure 57. Biodegradation chromatogram of reaction vessel 5 at 144 h

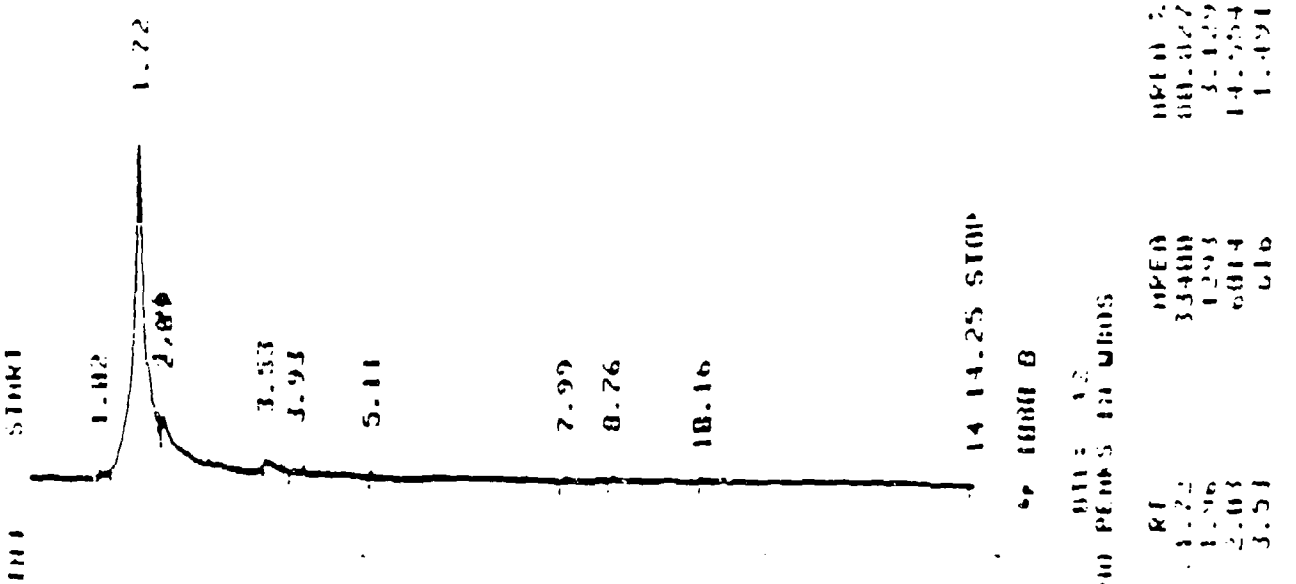


Figure 58. Biodegradation chromatogram of DNT blank at 168 h

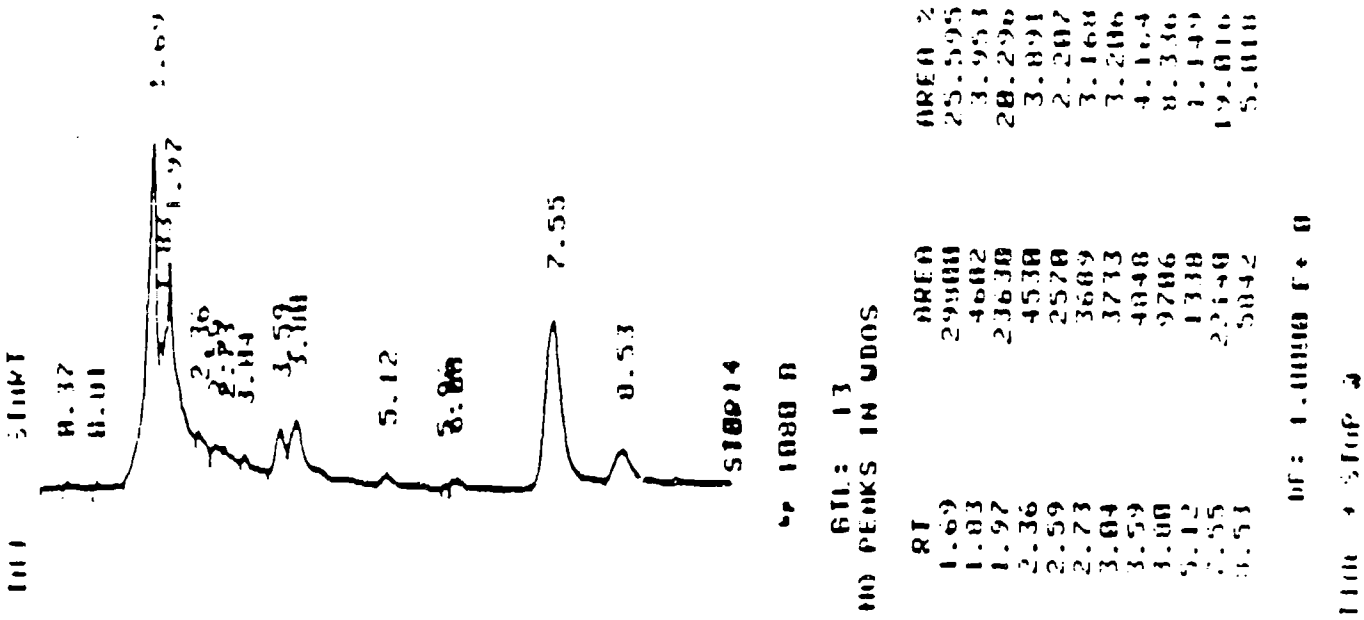


Figure 59. Biodegradation chromatogram of reaction vessel 1 at 168 h

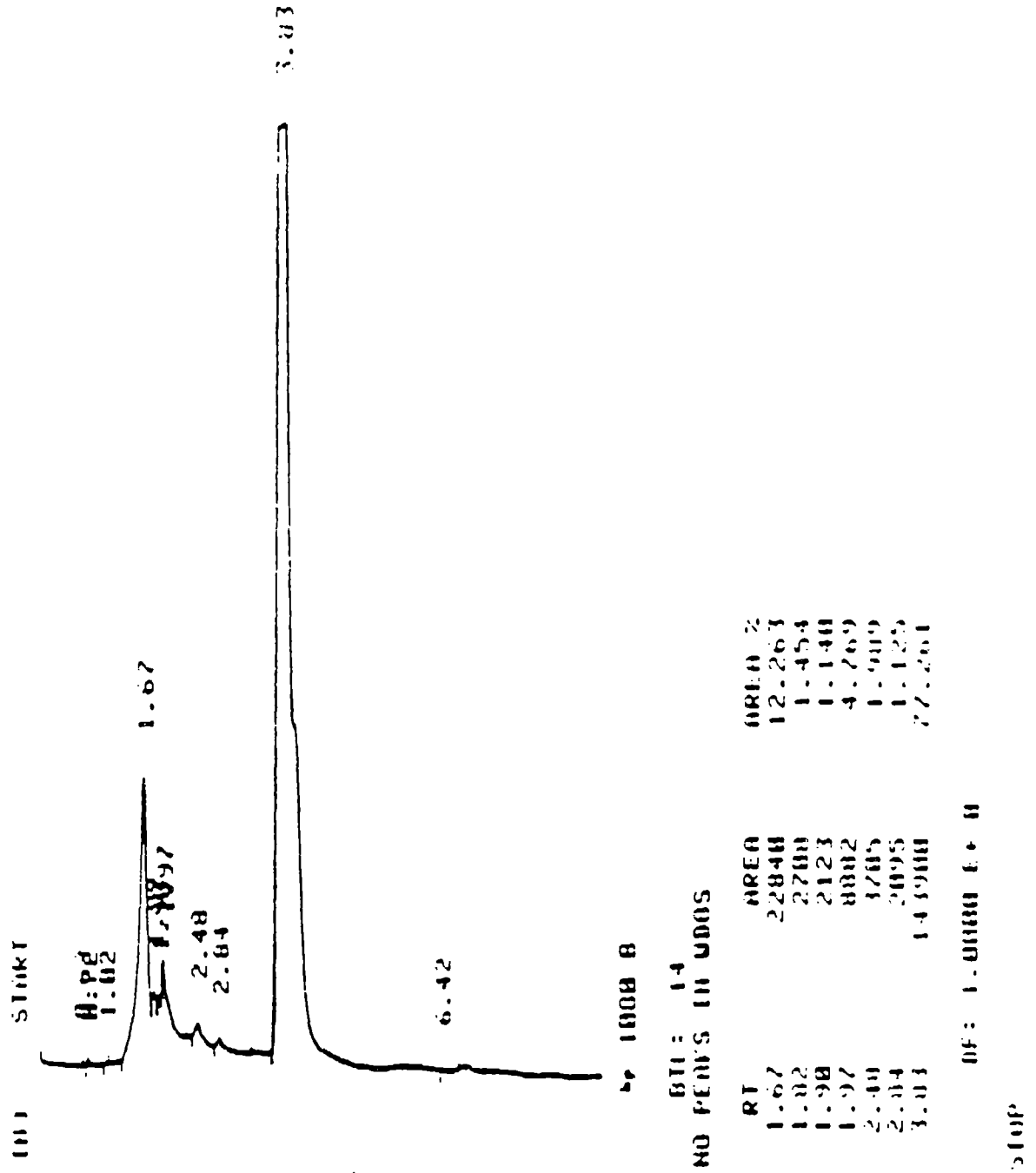


Figure 60. Biodegradation chromatogram of reaction vessel 2 at 168 h

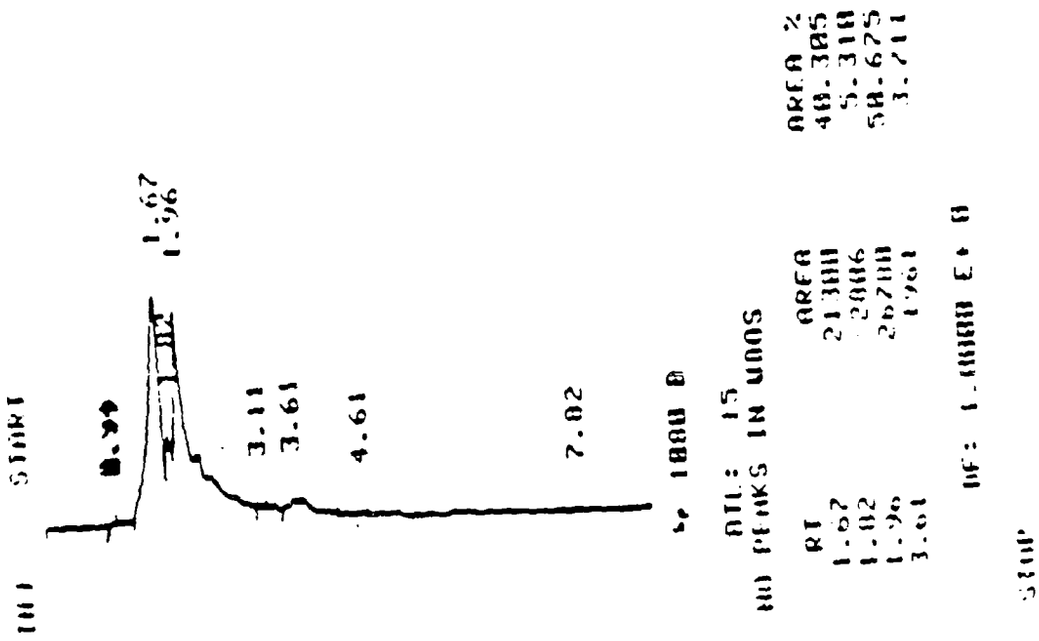


Figure 61. Biodegradation chromatogram of reaction vessel 3 at 168 h

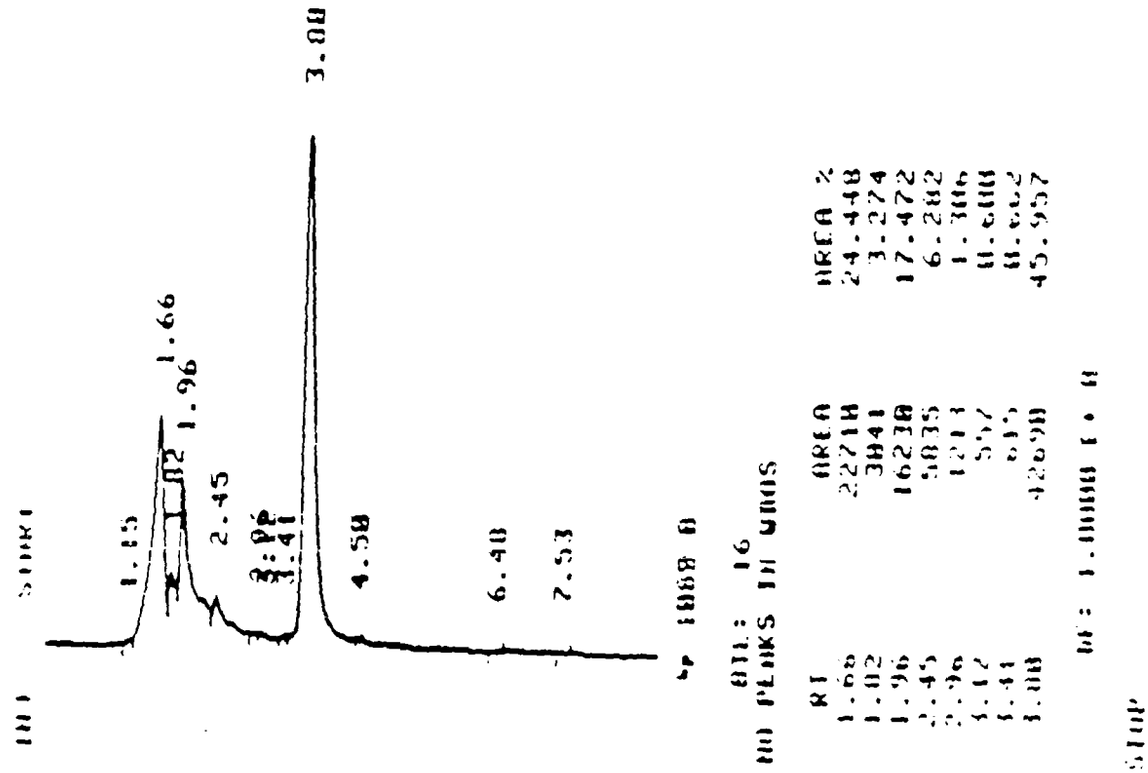


Figure 62. Biodegradation chromatogram of reaction vessel 4 at 168 h

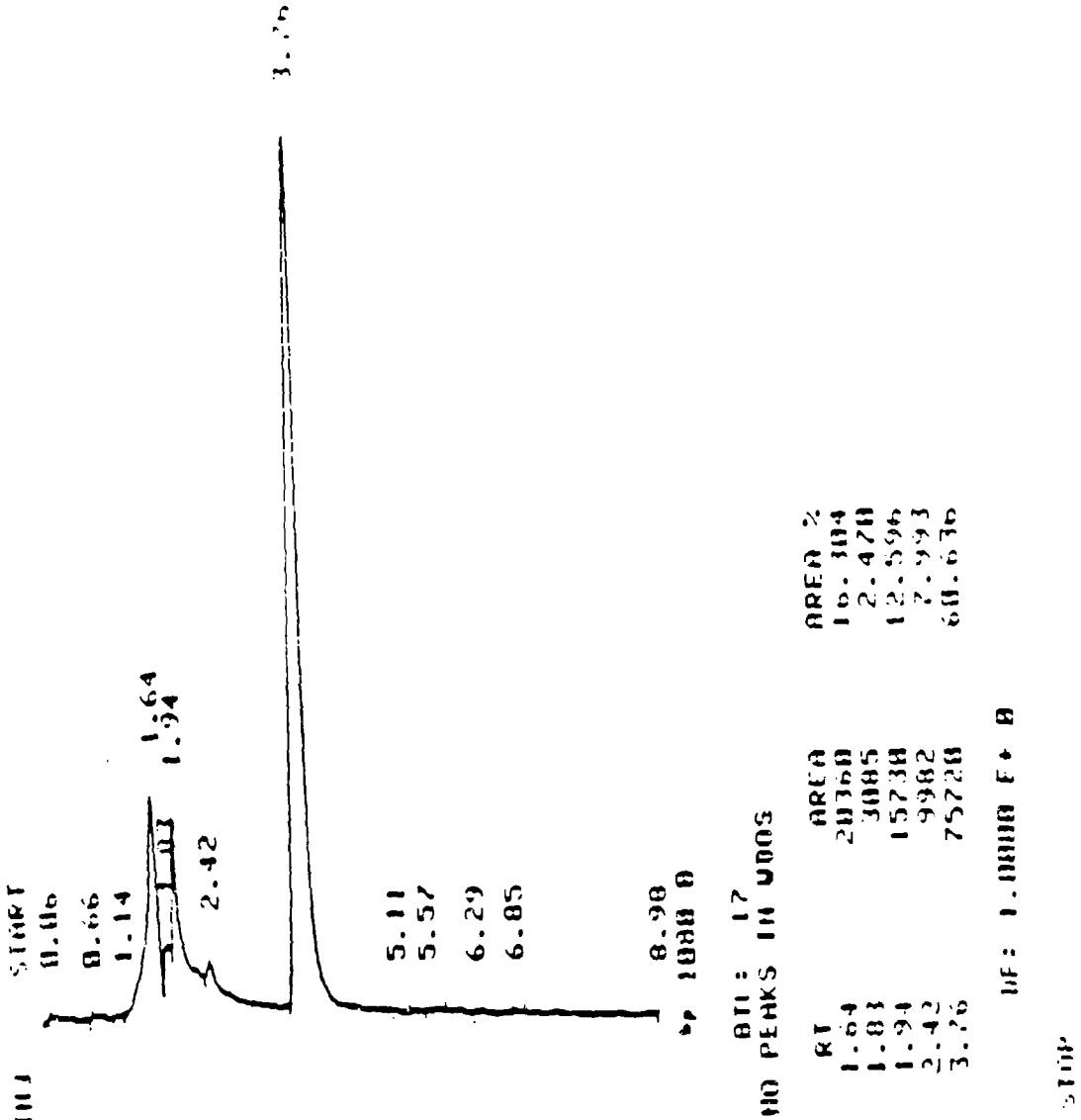


Figure 63. Biodegradation chromatogram of reaction vessel 5 at 168 h

Figure 64. Biodegradation chromatogram of reaction vessel 6 at 168 h

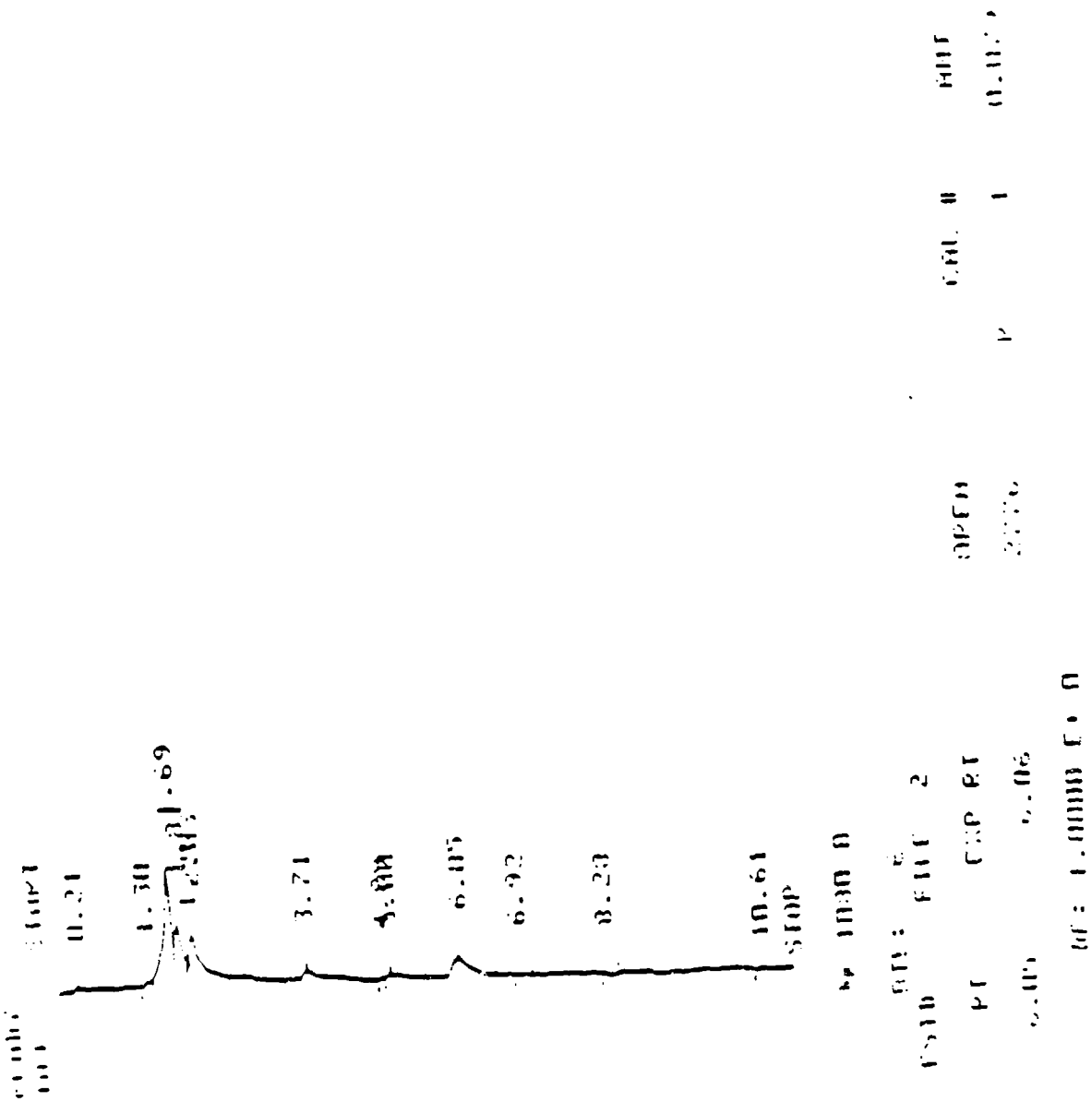


Figure 65. Biodegradation chromatogram of reaction vessel 1 at 22 h

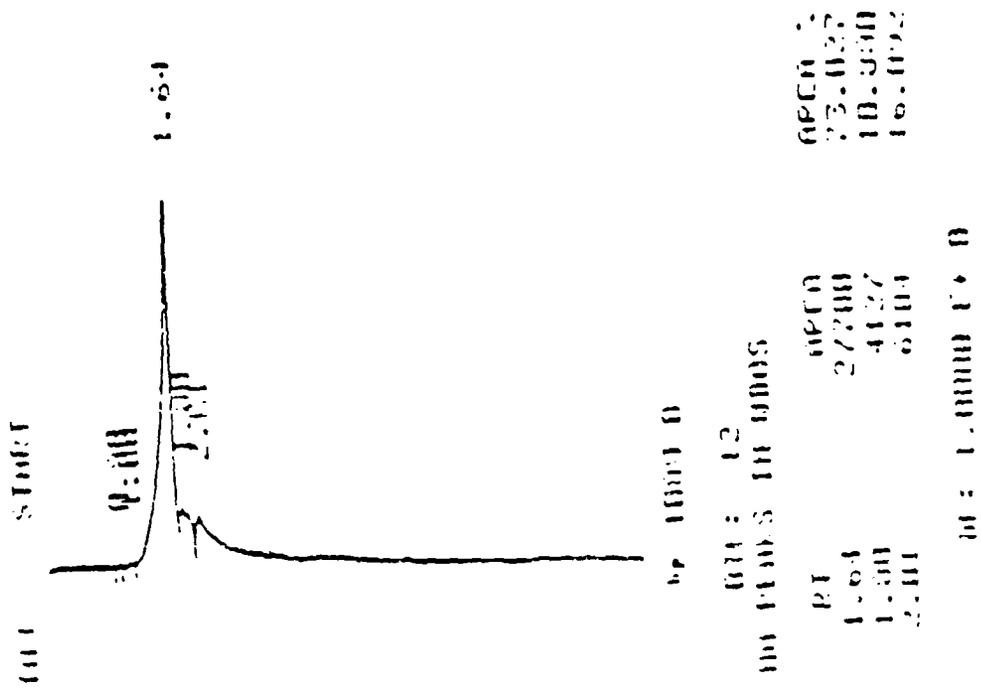


Figure 66. Biodegradation chromatogram of reaction vessel 2 at 94 h

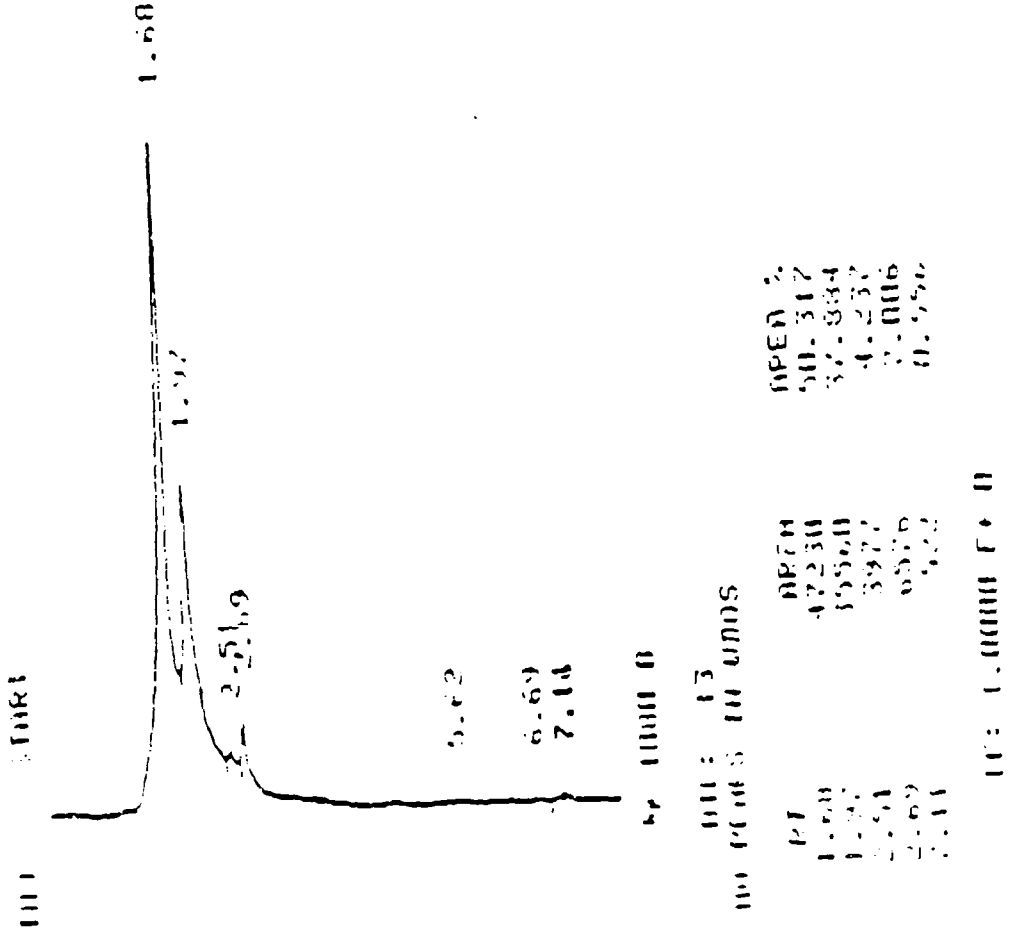


Figure 67. Biodegradation chromatogram of reaction vessel 3 at 118 h

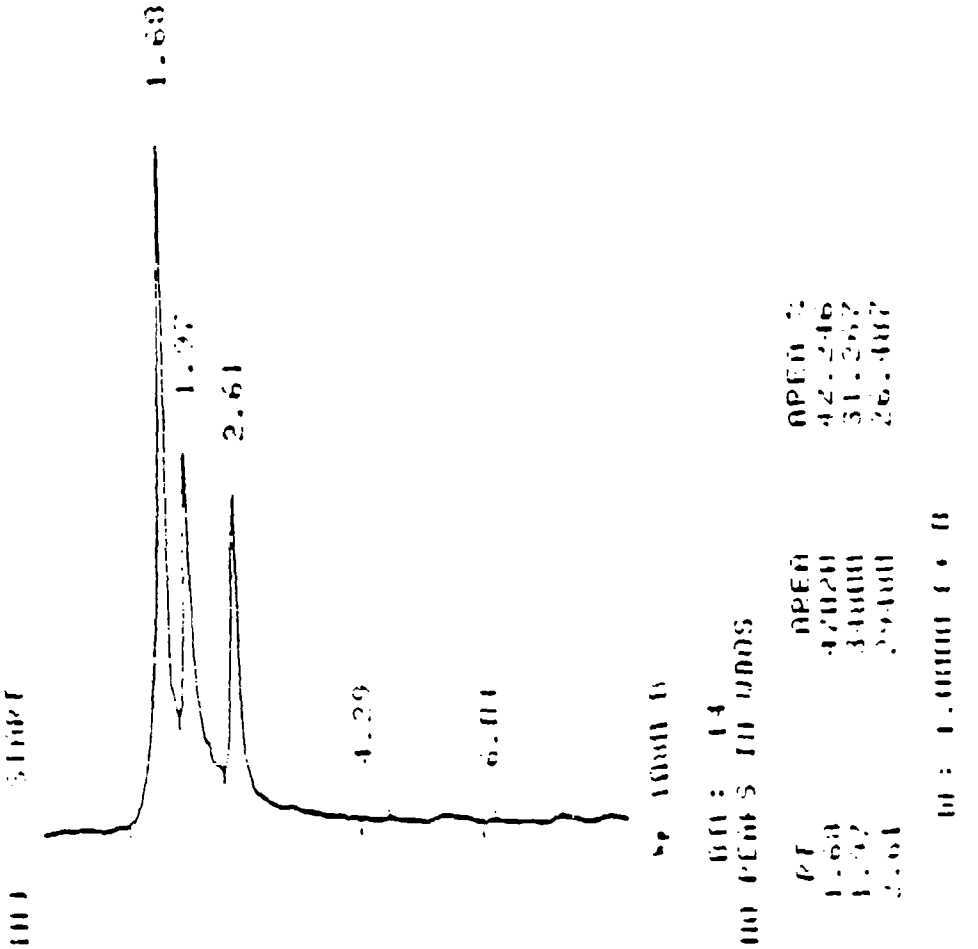


Figure 68. Biodegradation chromatogram of reaction vessel 4 at 142 h

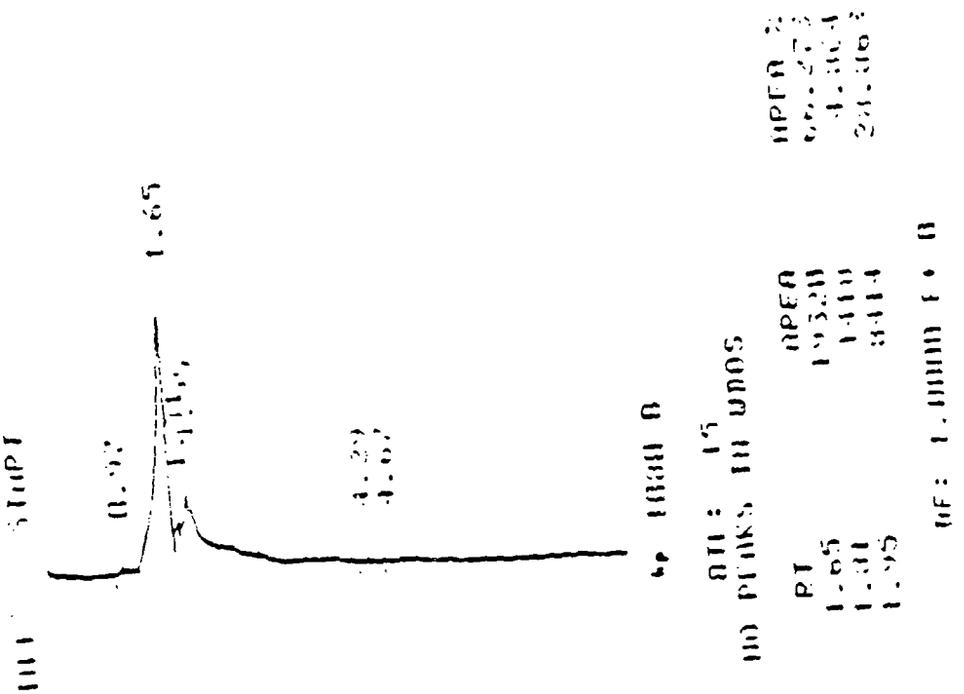


Figure 69. Biodegradation chromatogram of reaction vessel 5 at 166 h

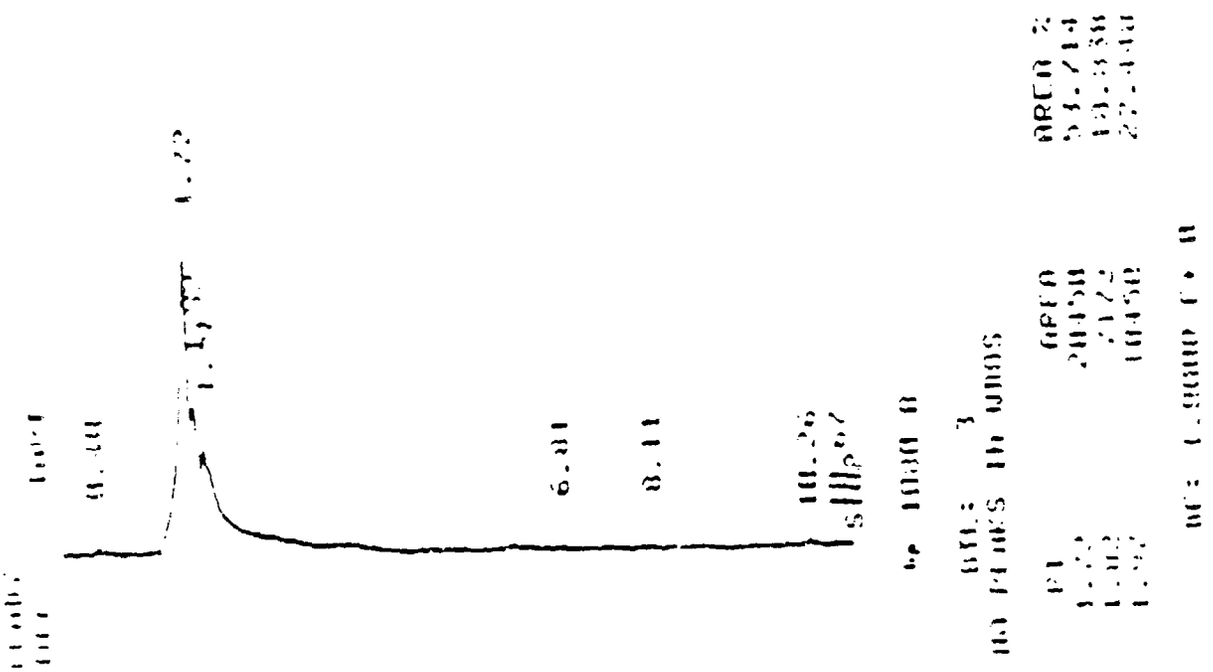


Figure 7C. Biodegradation chromatogram of reaction vessel 6 at 190 h

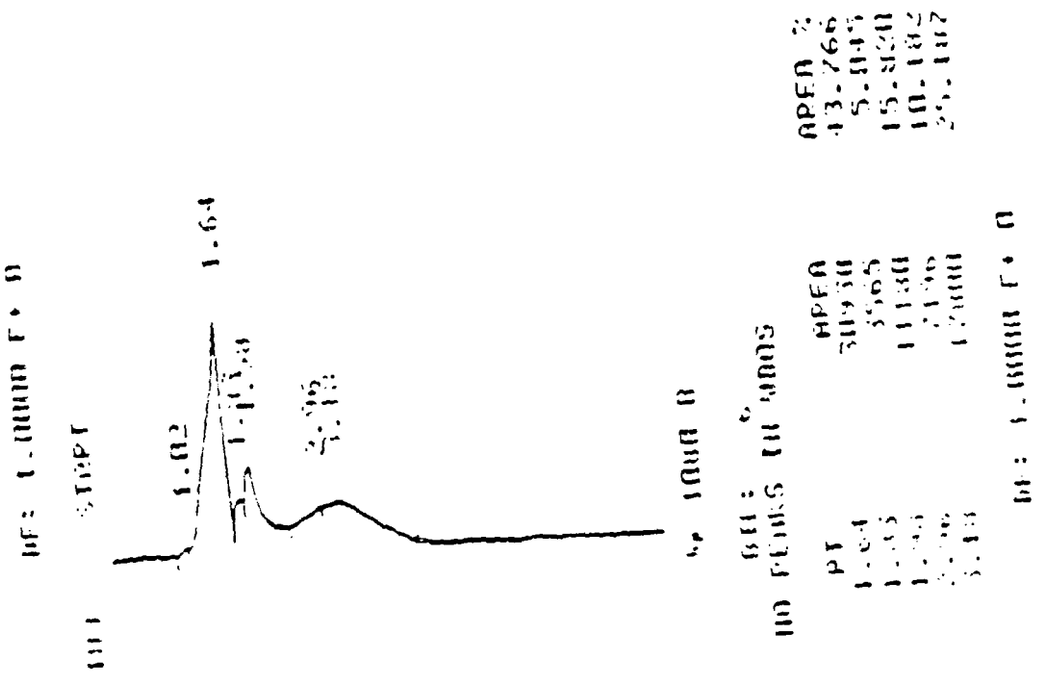


Figure 71. Biodegradation chromatogram of nutrient water at 264 h

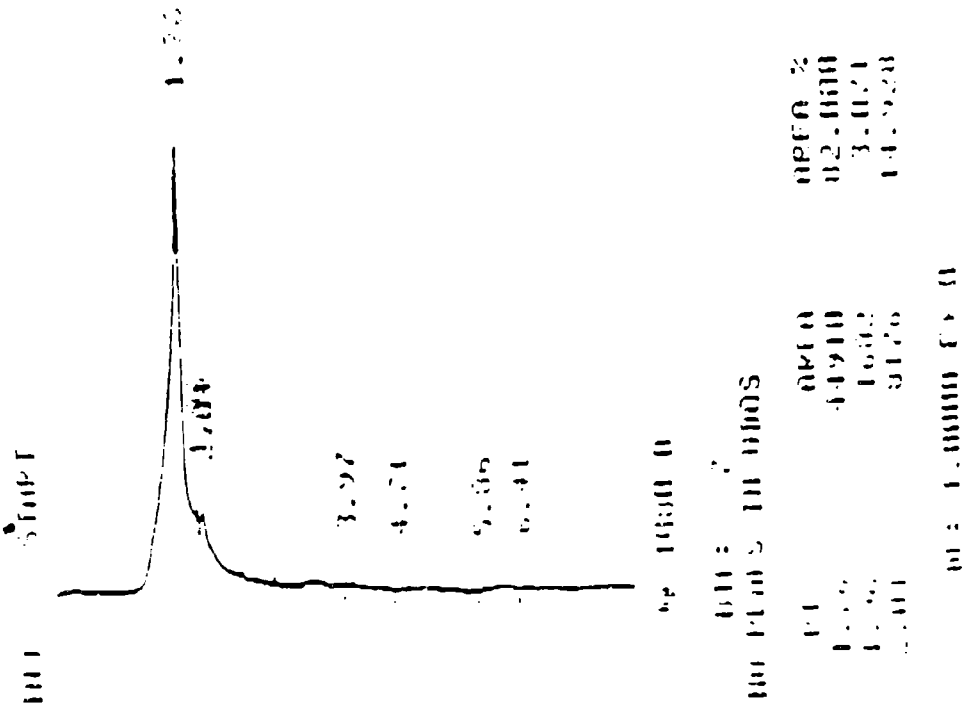


Figure 72. Biodegradation chromatogram of reaction vessel 1 at 264 h

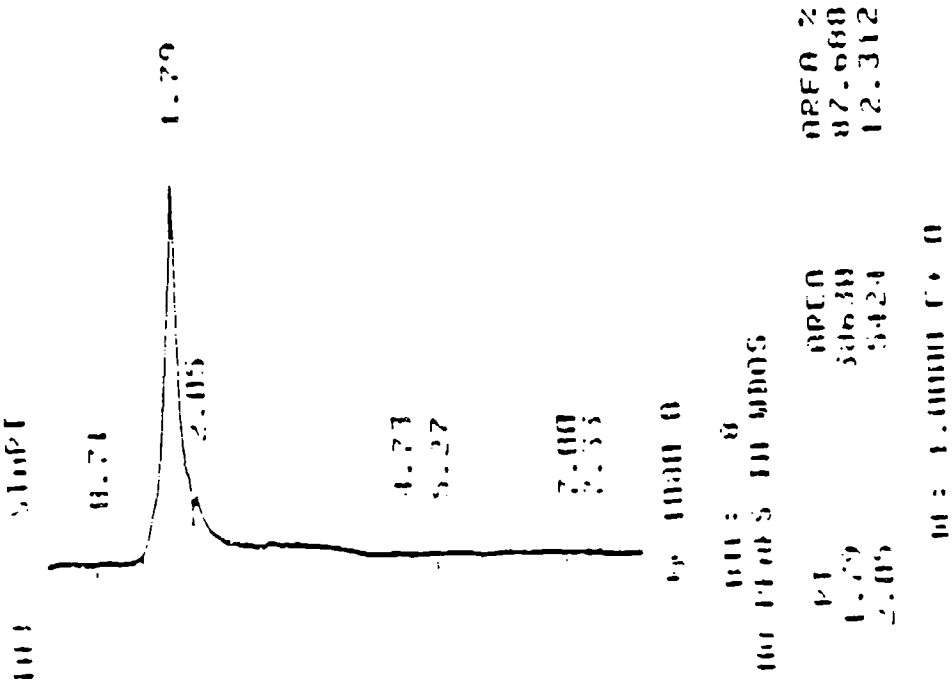


Figure 73. Biodegradation chromatogram of reaction vessel 2 at 264 h

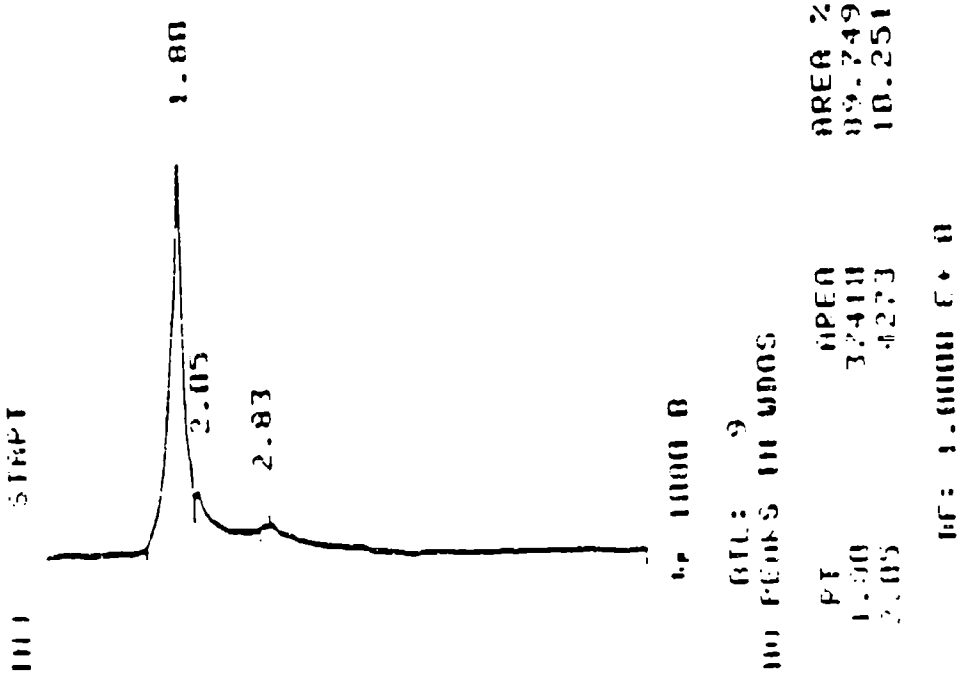


Figure 74. Biodegradation chromatogram of reaction vessel 3 at 264 h

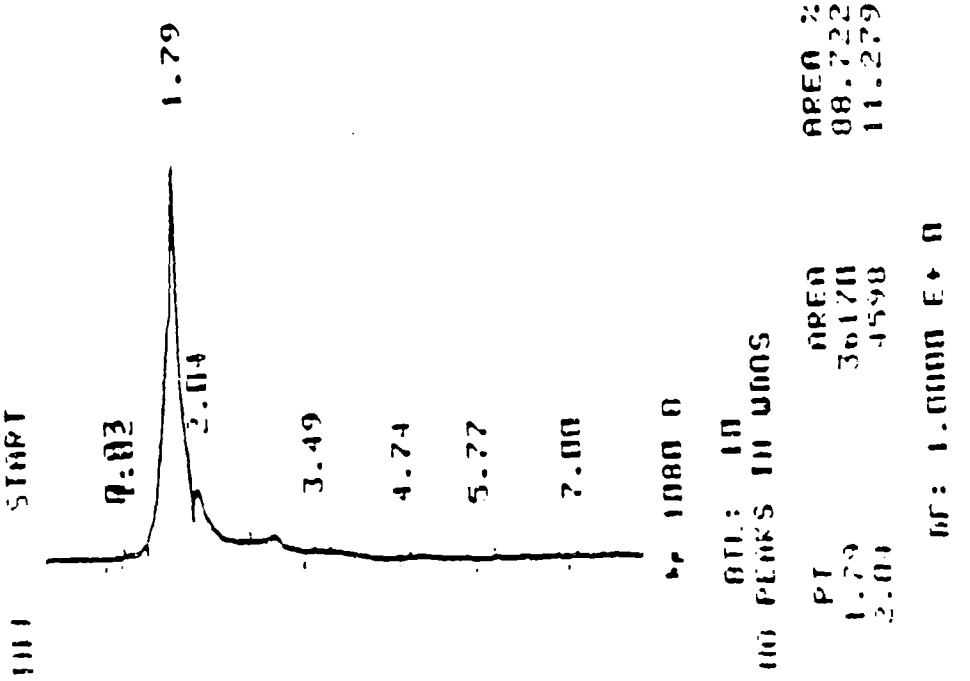


Figure 75. Biodegradation chromatogram of reaction vessel 4 at 264 h

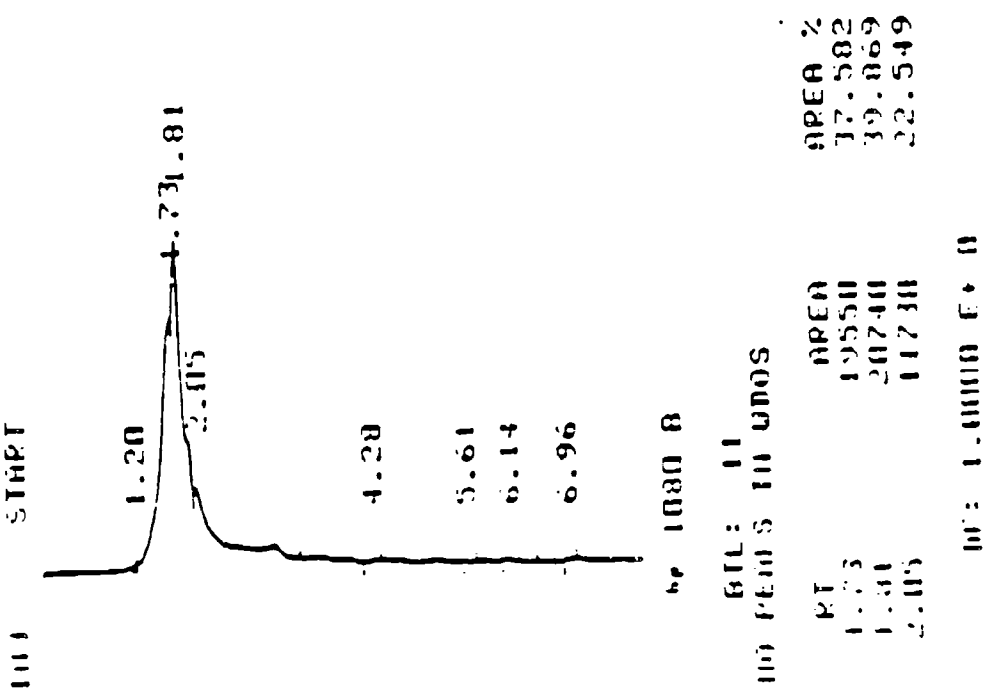


Figure 76. Biodegradation chromatogram of reaction vessel 5 at 264 h

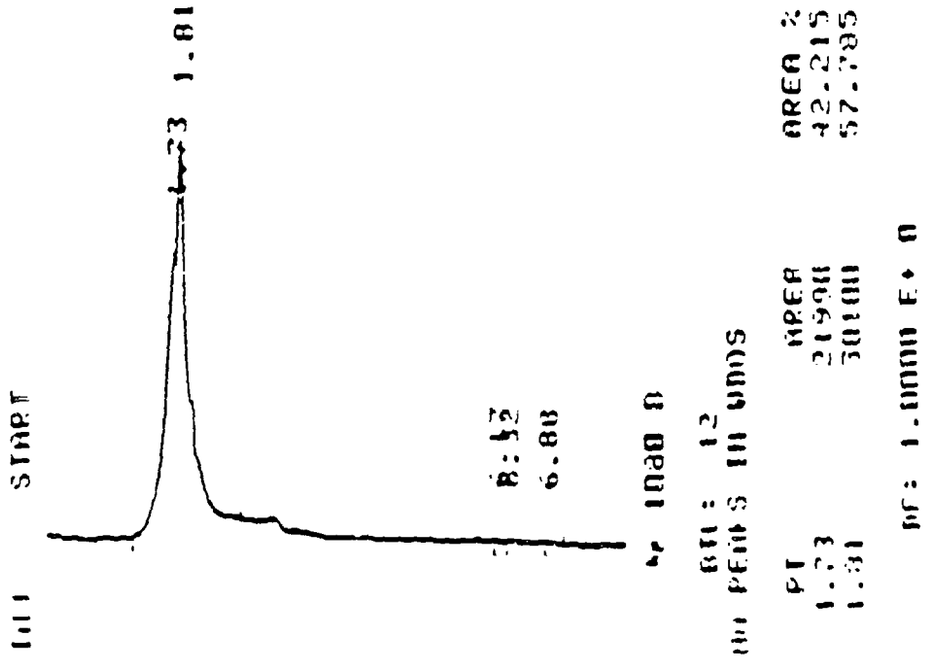


Figure 77. Biodegradation chromatogram of reaction vessel 6 at 264 h

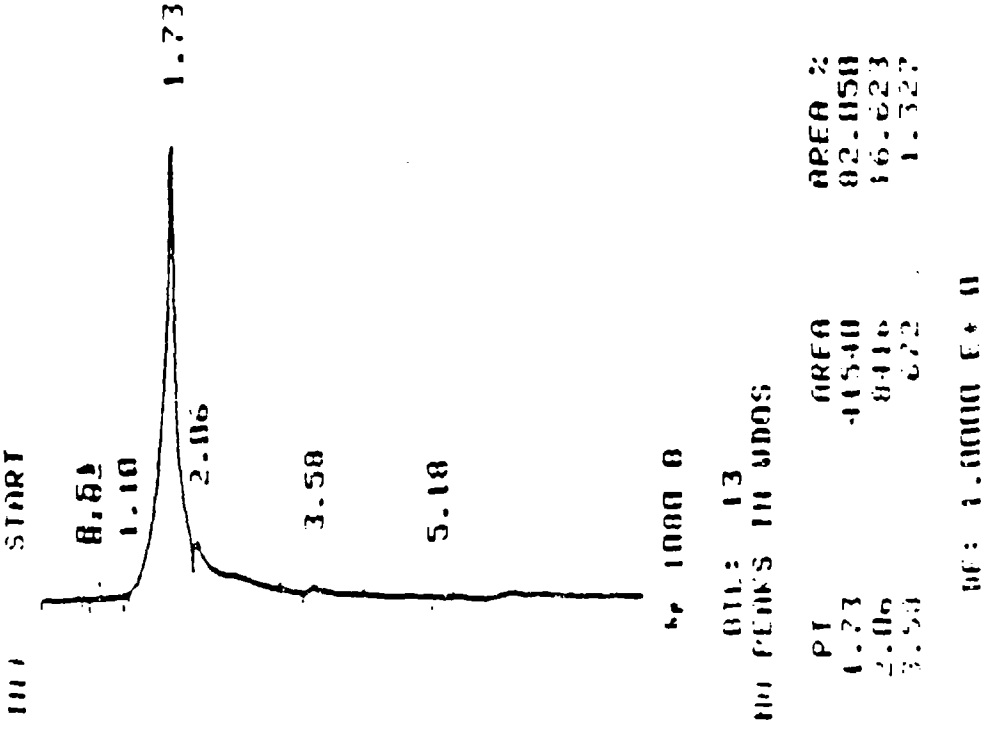


Figure 78. Biodegradation chromatogram of reaction vessel 7 at 264 h

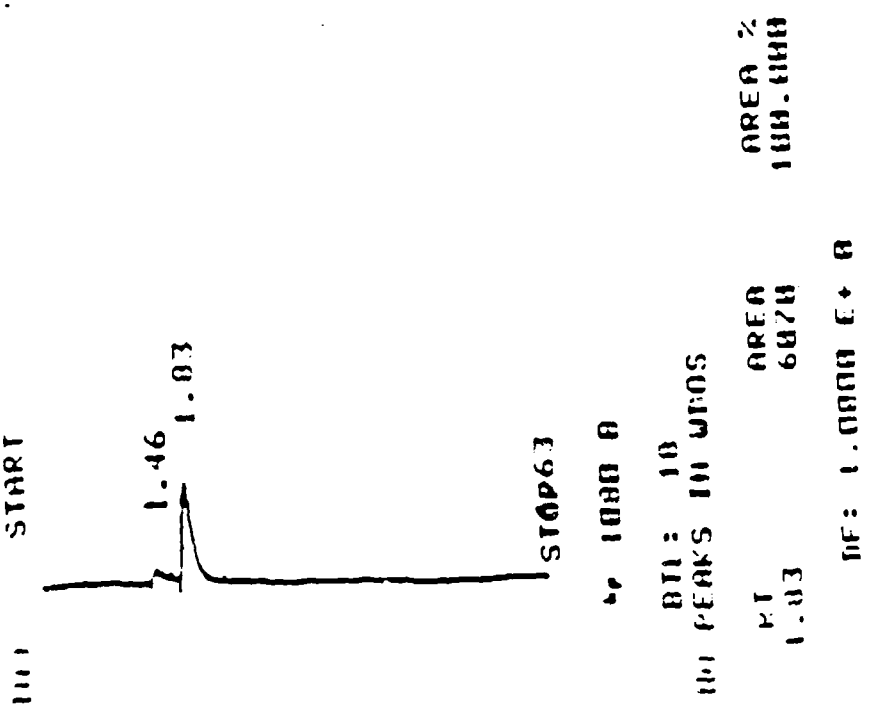


Figure 79. Biodegradation chromatogram of seed at 0 h

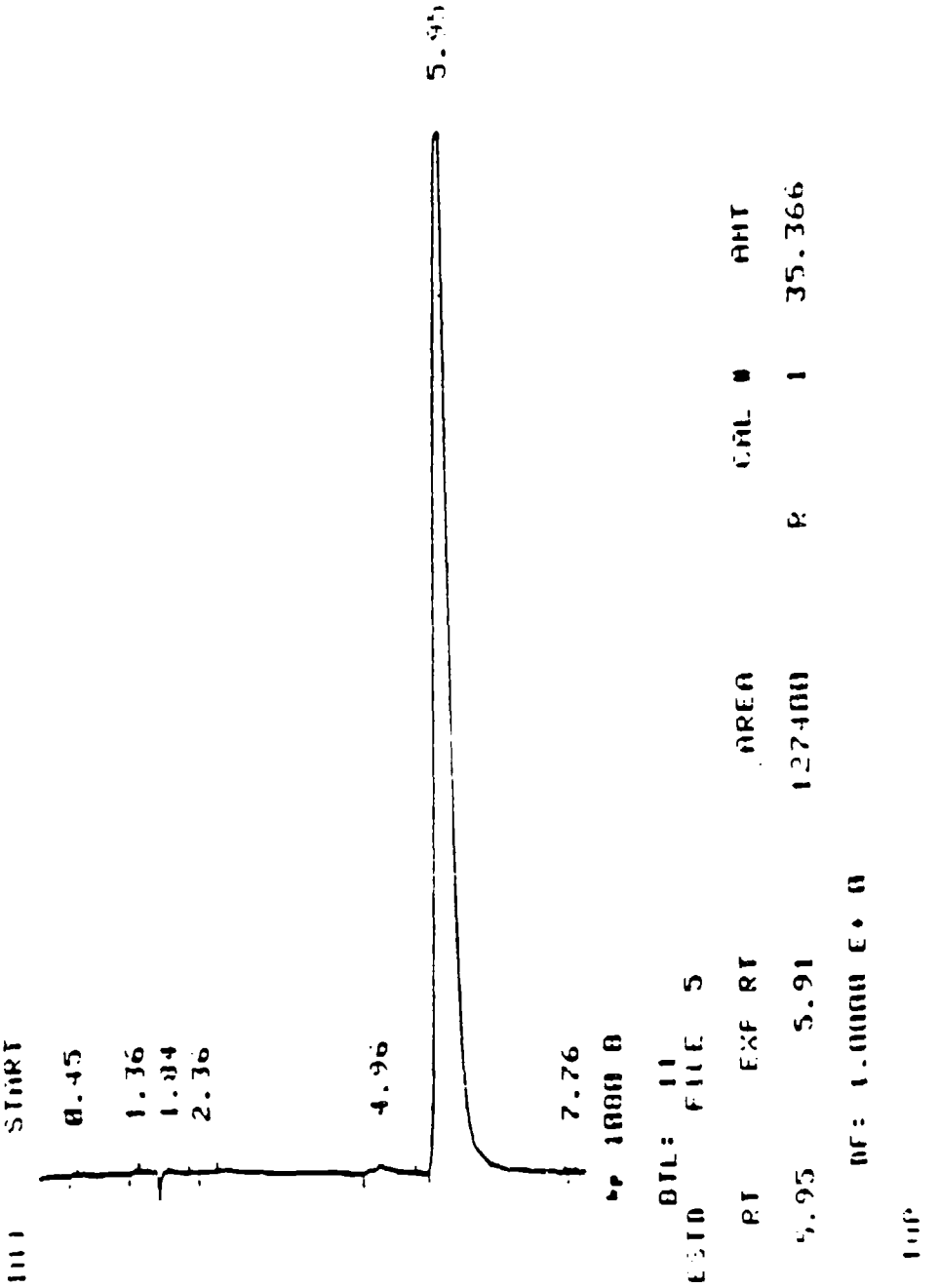


Figure 80. Biodegradation chromatogram of nutrient water at 0 h

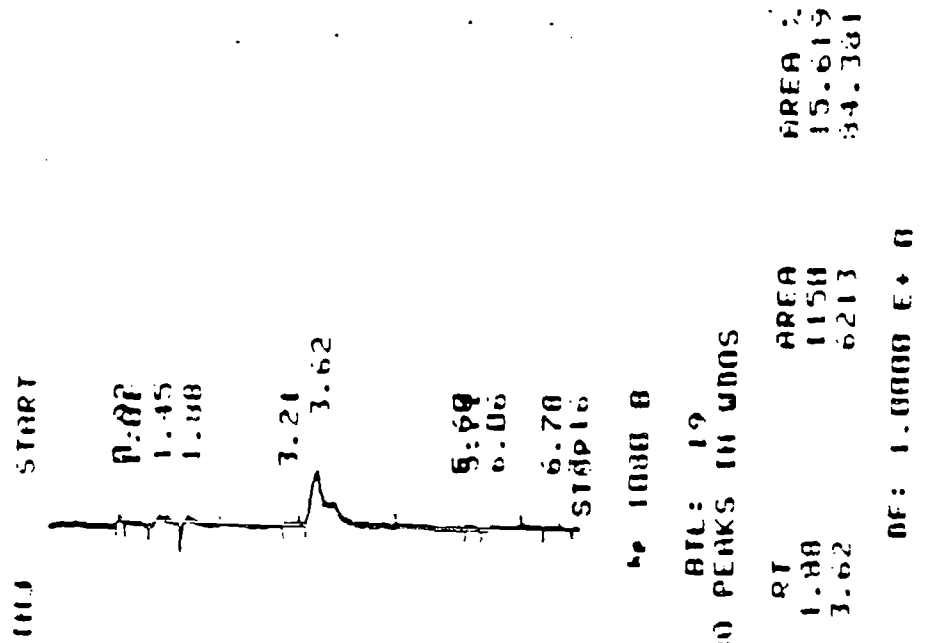


Figure 81. Biodegradation chromatogram of reaction vessel 1 at 24 h

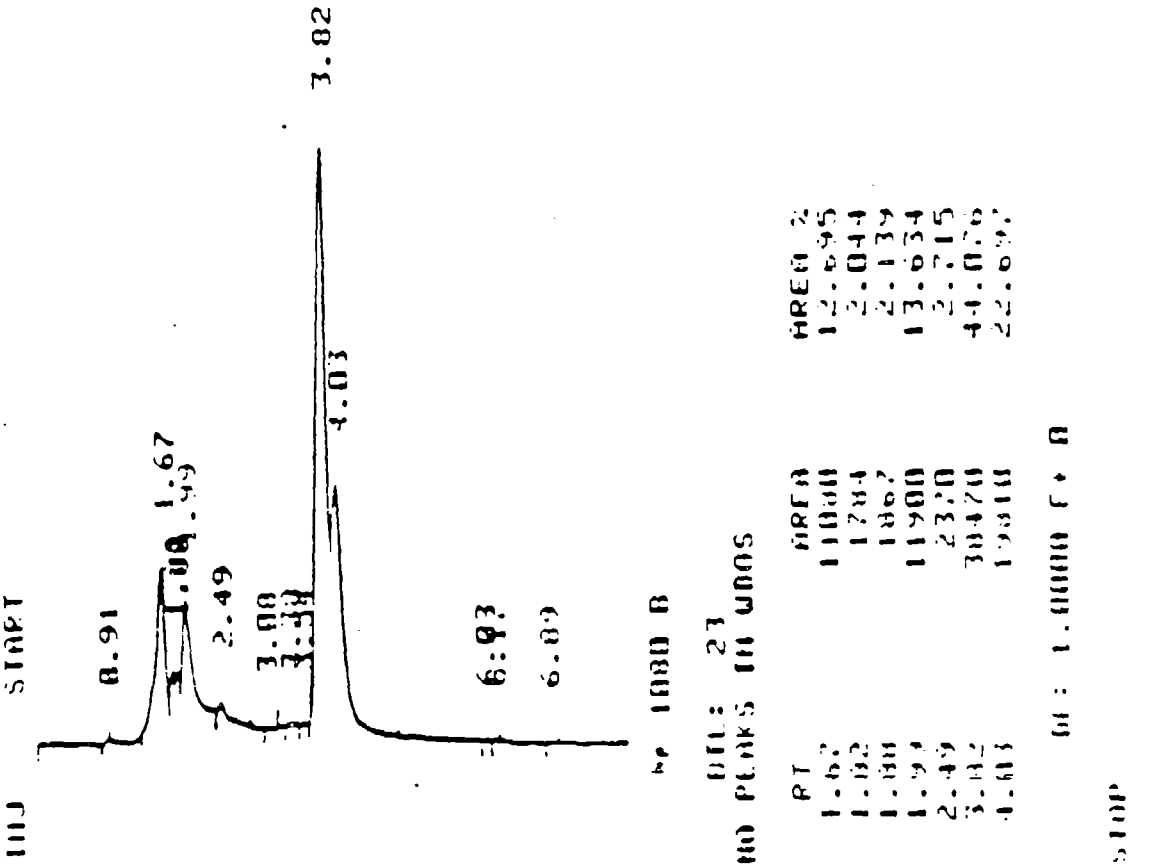


Figure 82. Biodegradation chromatogram of reaction vessel 2 at 48 h

Figure 83. Biodegradation chromatogram of reaction vessel 4 at 170 h

Figure 84. Biodegradation chromatogram of reaction vessel 5 at 216 h

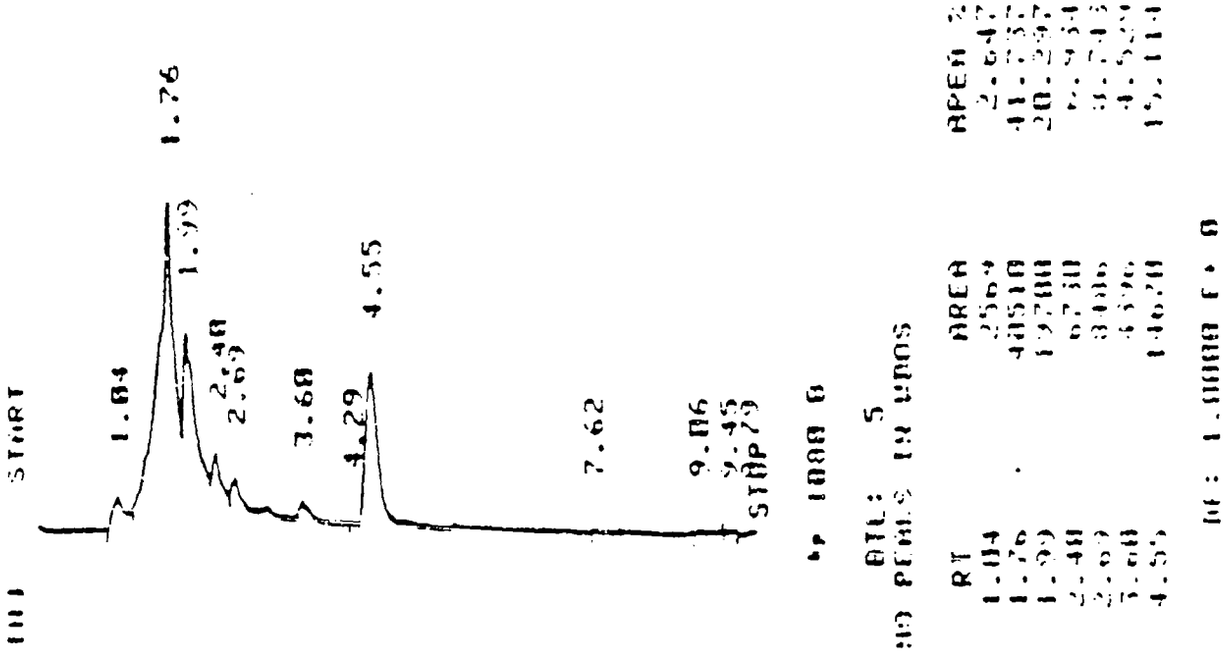


Figure 85. Biodegradation chromatogram of reaction vessel 6 at 264 h

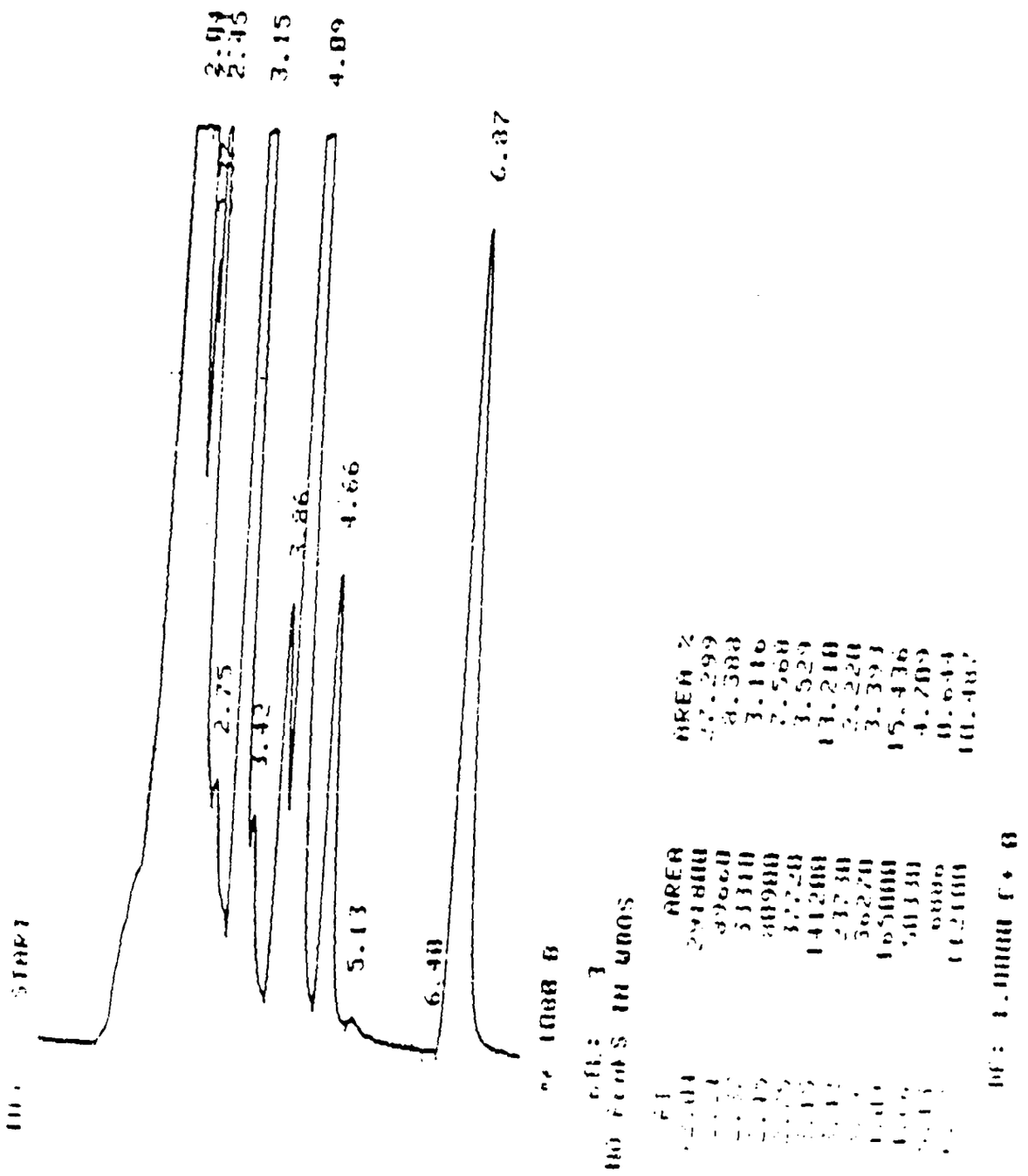


Figure 86. Biodegradation chromatogram of seed at 337 h

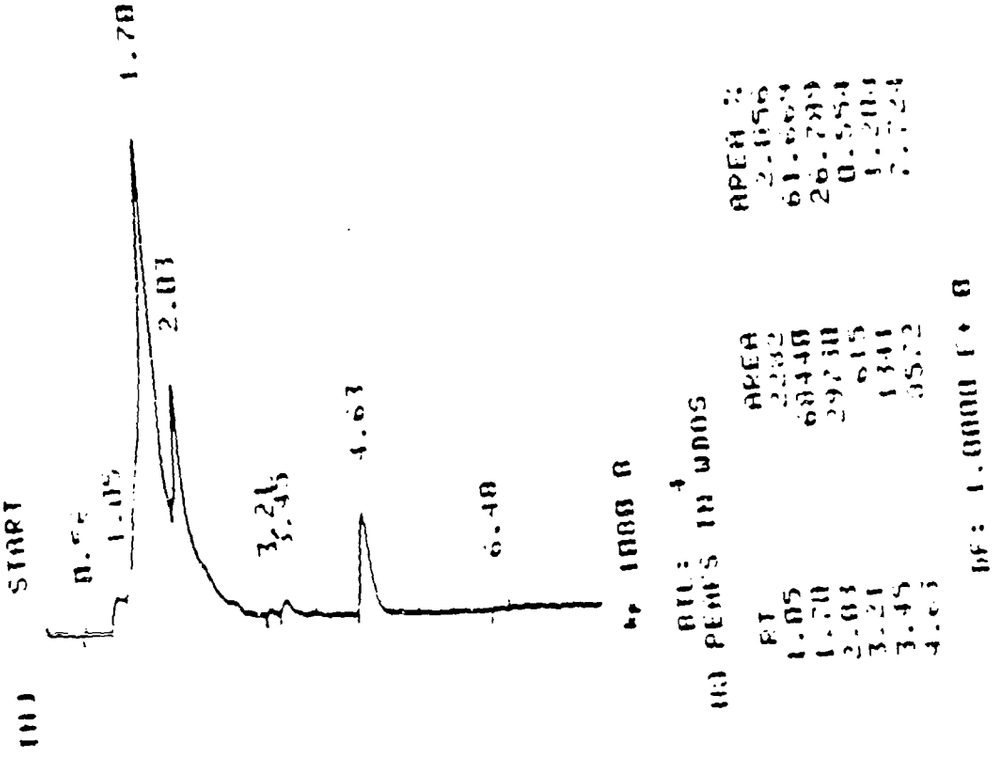


Figure 87. Biodegradation chromatogram of nutrient water at 337 h

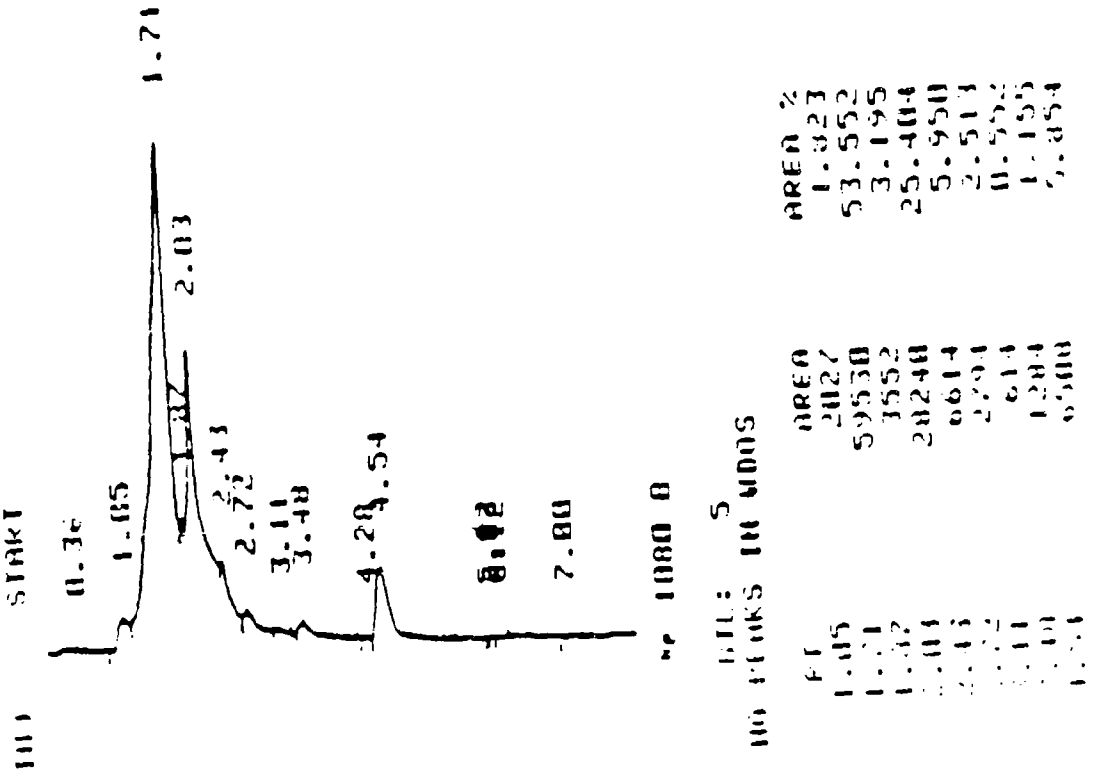


Figure 88. Biodegradation chromatogram of reaction vessel 1 at 337 h

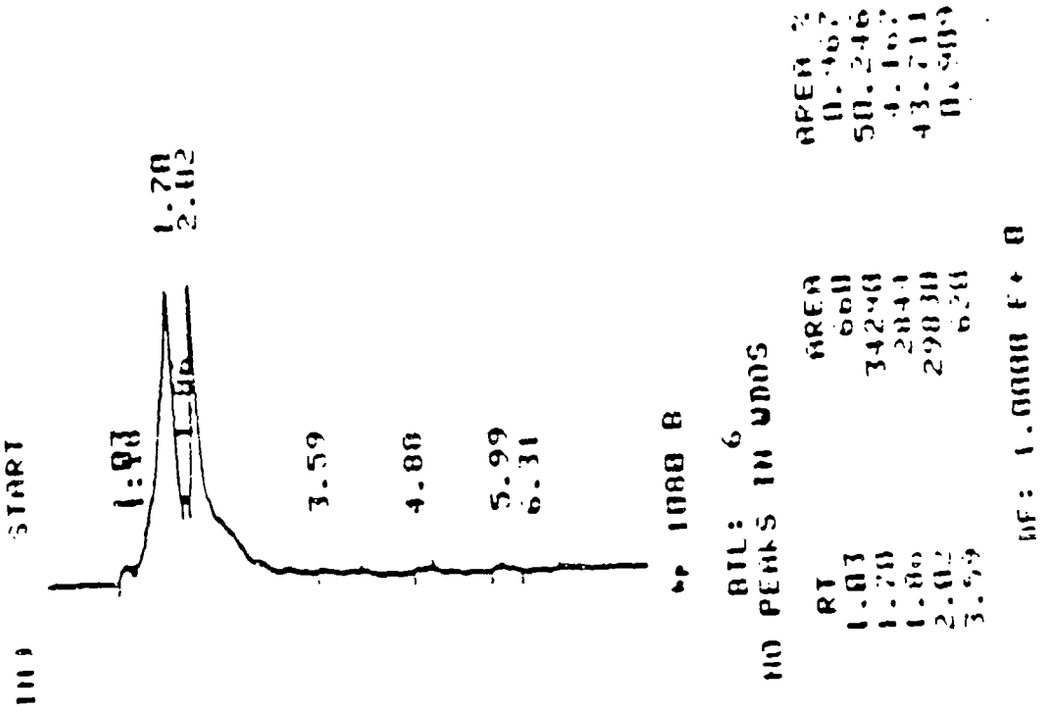


Figure 89. Biodegradation chromatogram of reaction vessel 2 at 337 h

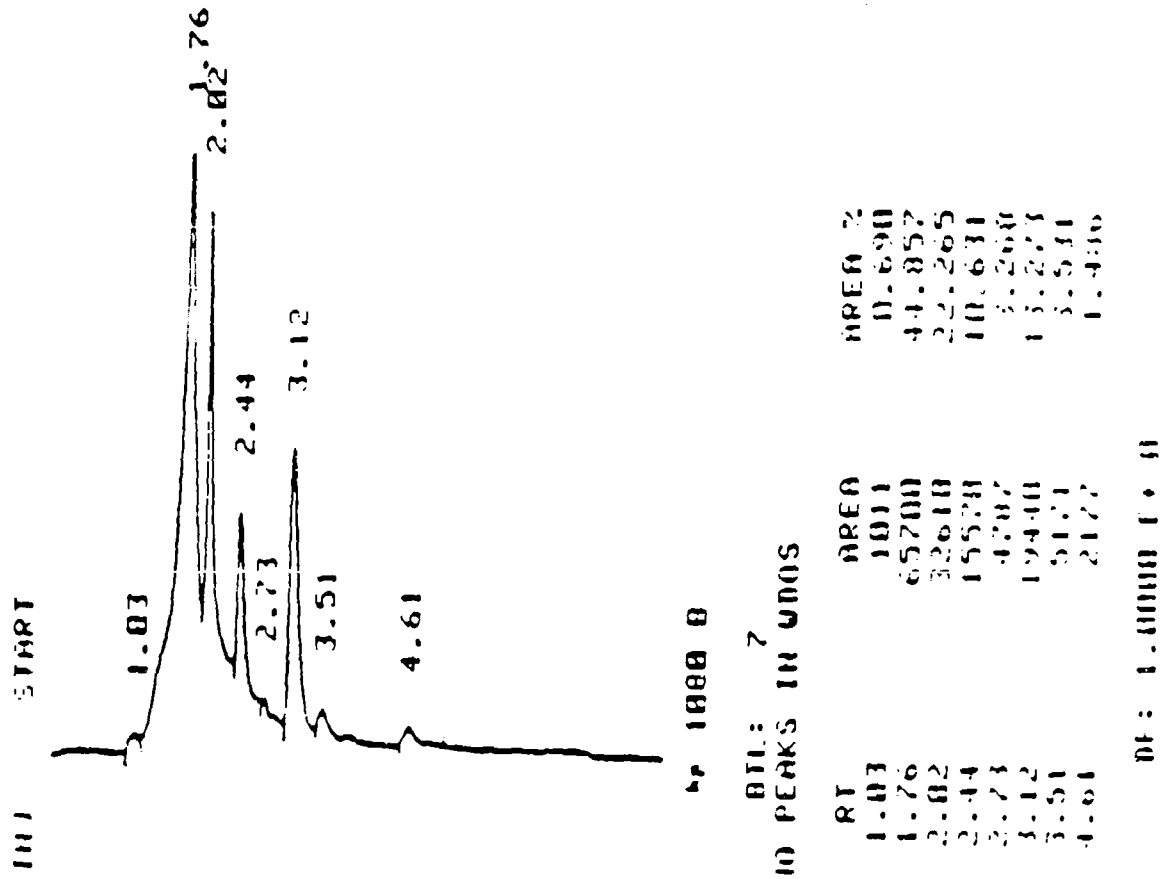


Figure 90. Biodegradation chromatogram of reaction vessel 3 at 337 h

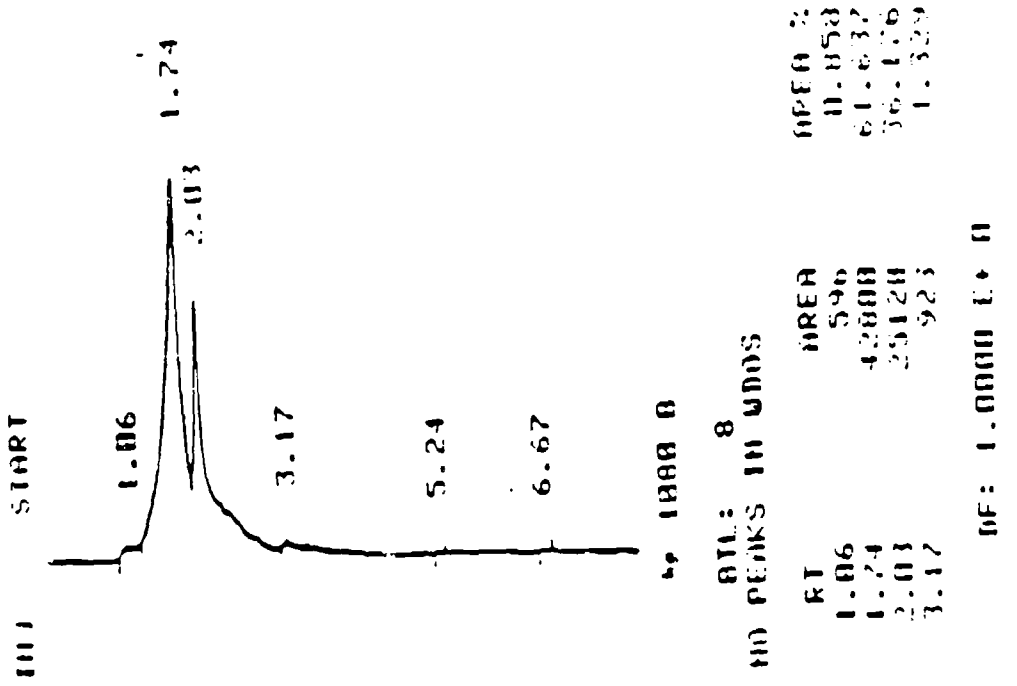


Figure 91. Biodegradation chromatogram of reaction vessel 4 at 337 h

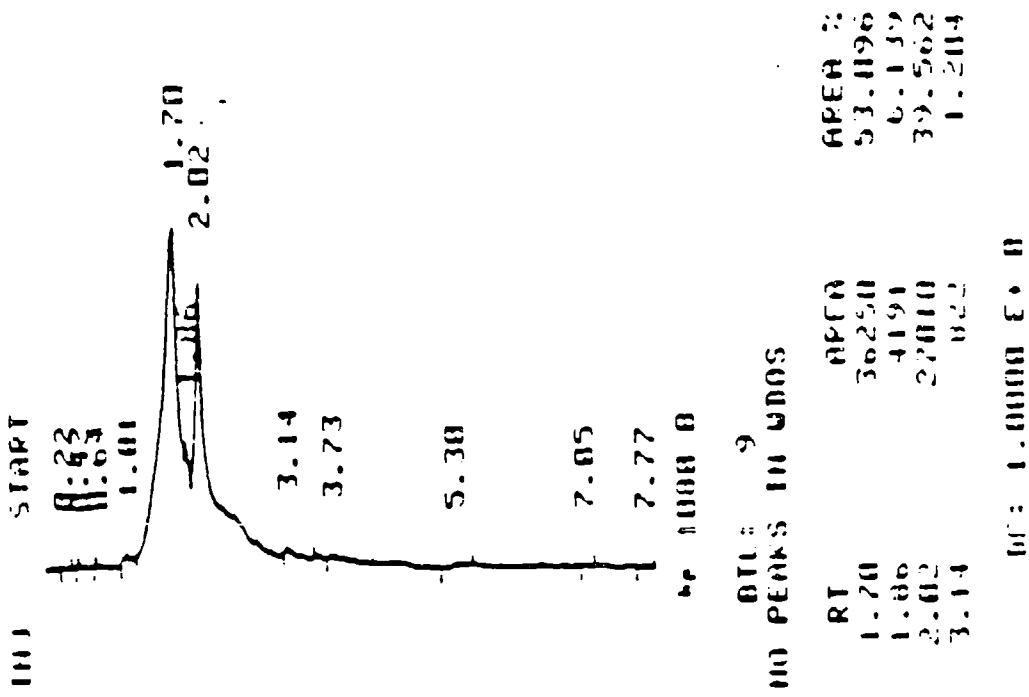
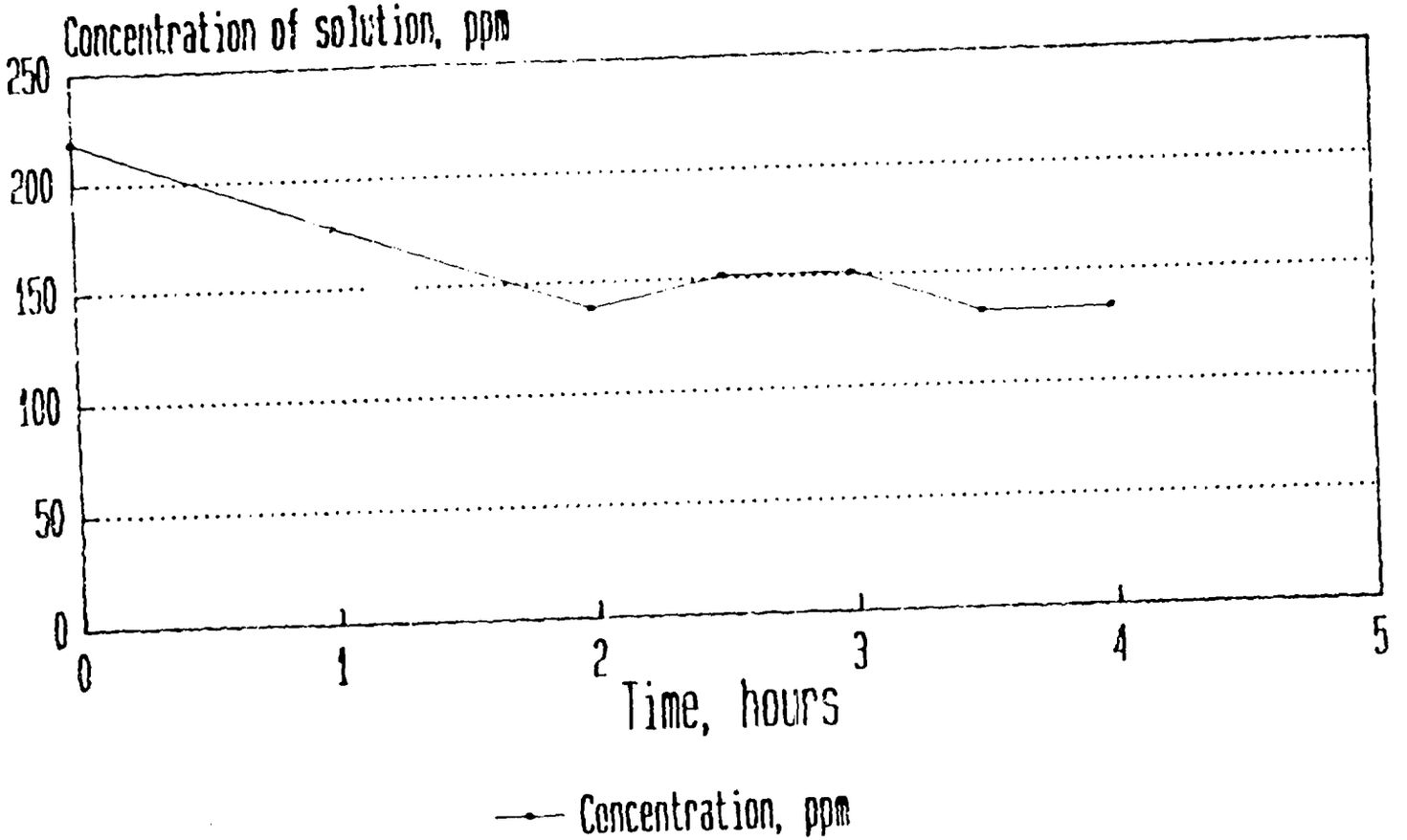


Figure 92. Biodegradation chromatogram of reaction vessel 5 at 337 h

Figure 93. Biodegradation chromatogram of reaction vessel 6 at 337 h

Figure 94. Biodegradation chromatogram of reaction vessel 7 at 337 h



Initial Concentration=219 ppm

Figure 95. Adsorption of DNf by FS-400
Optimization of time

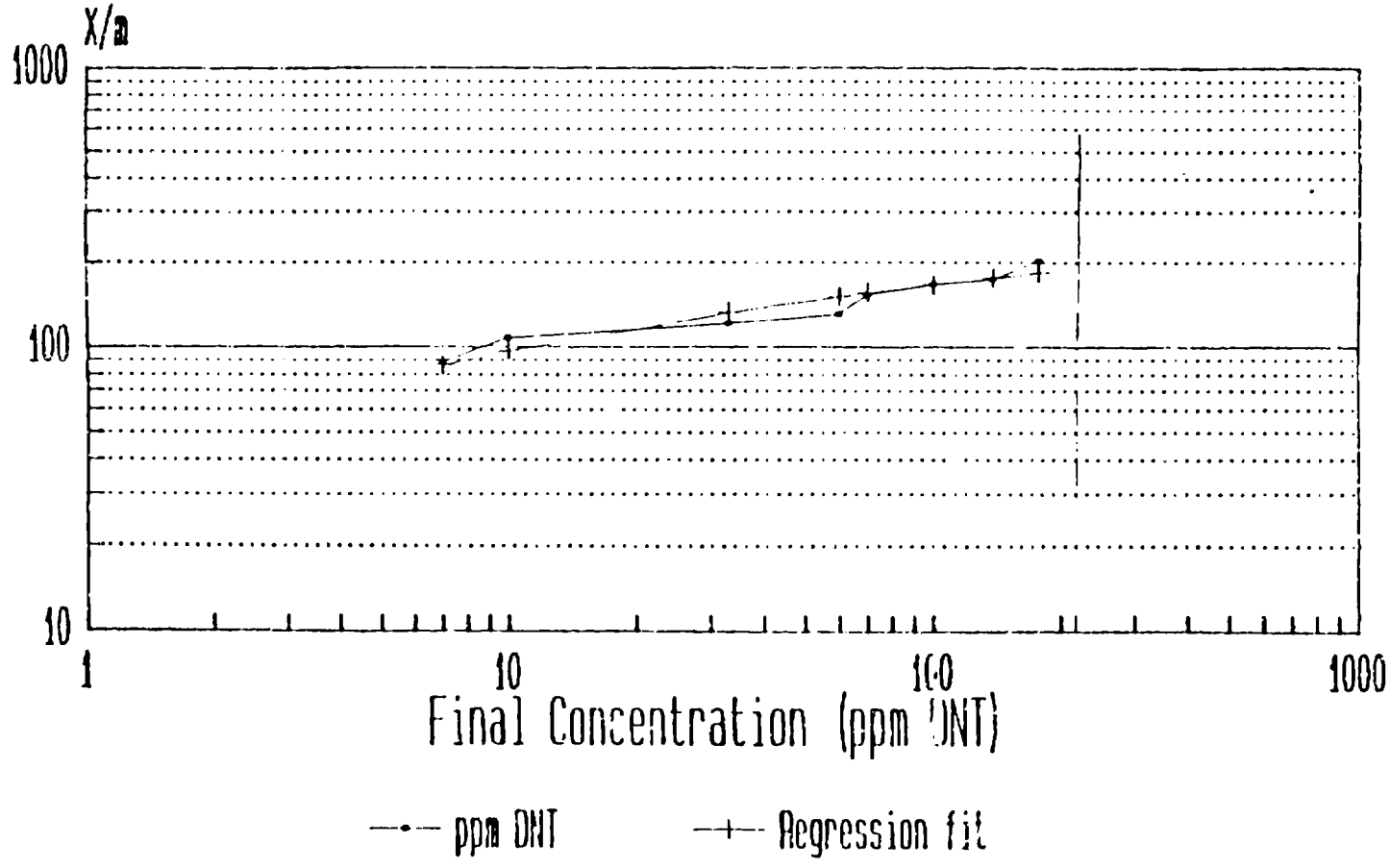
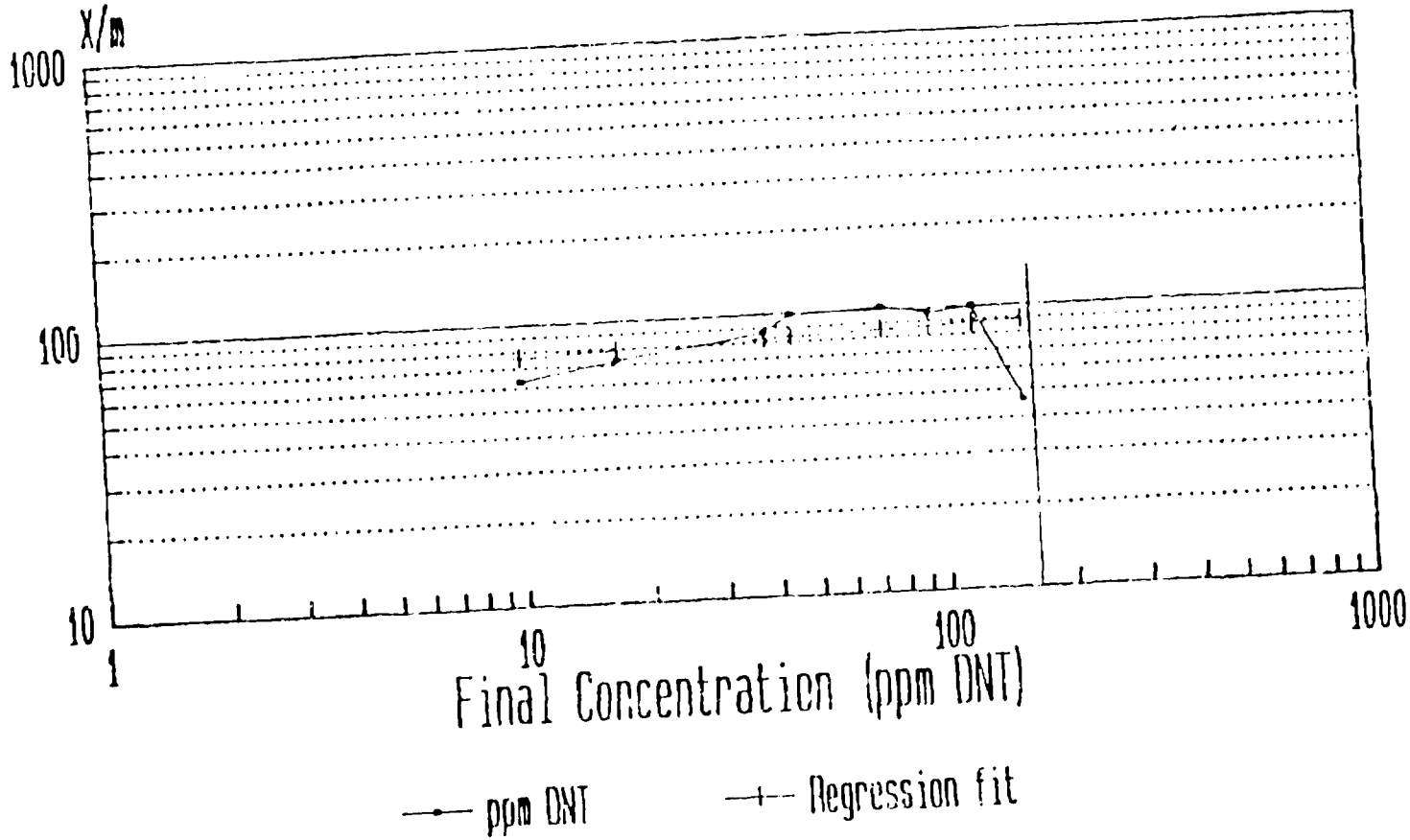


Figure 96. Adsorption isotherms (FS-400)
Water dry wastewater



X/m = mg DNT/g Carbon

Figure 97. Adsorption isotherms (FS-400)
Solvent rich water dry wastewater

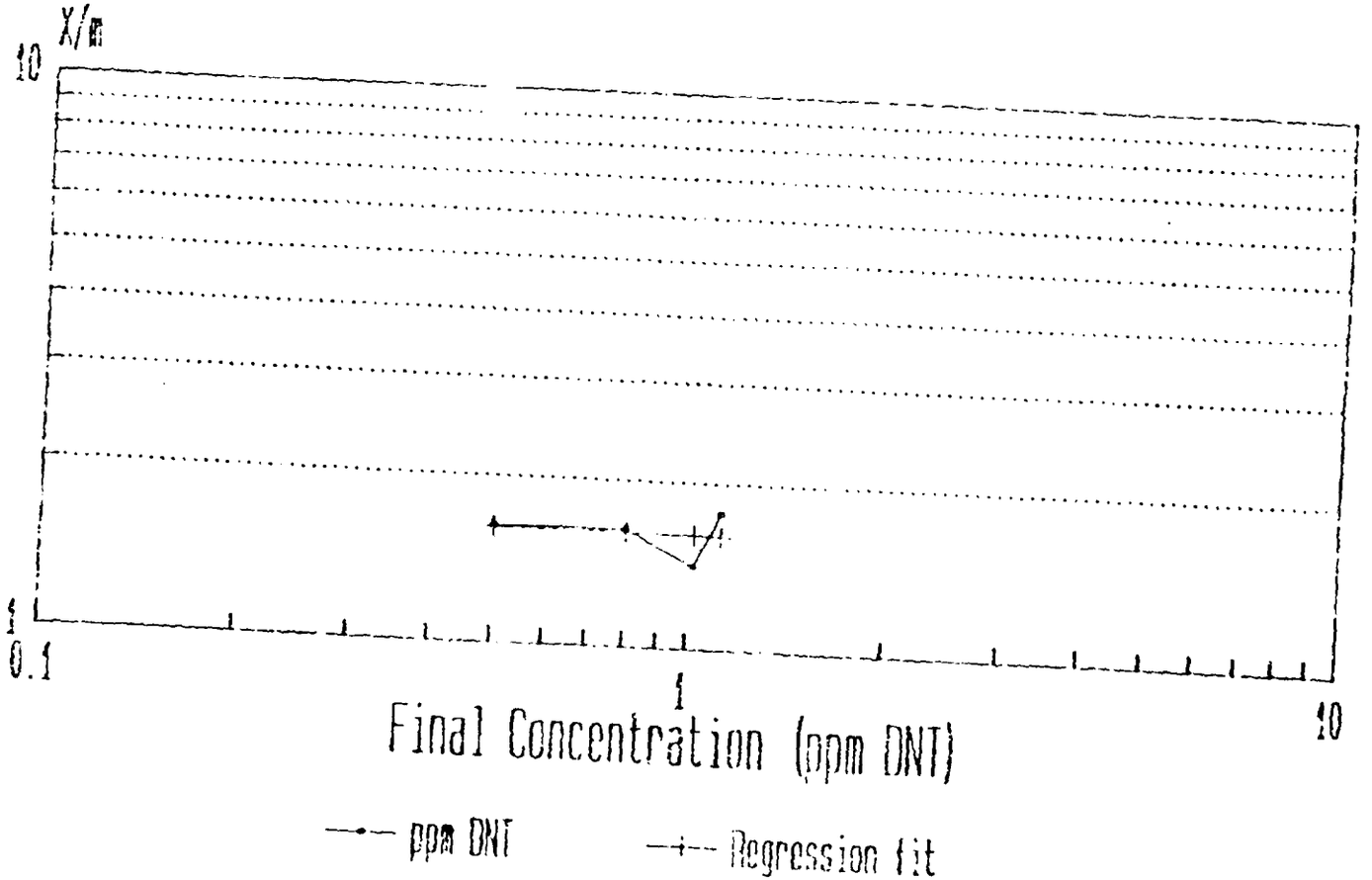


Figure 98. Adsorption isotherms (FS-400)
Plant effluent + DNT

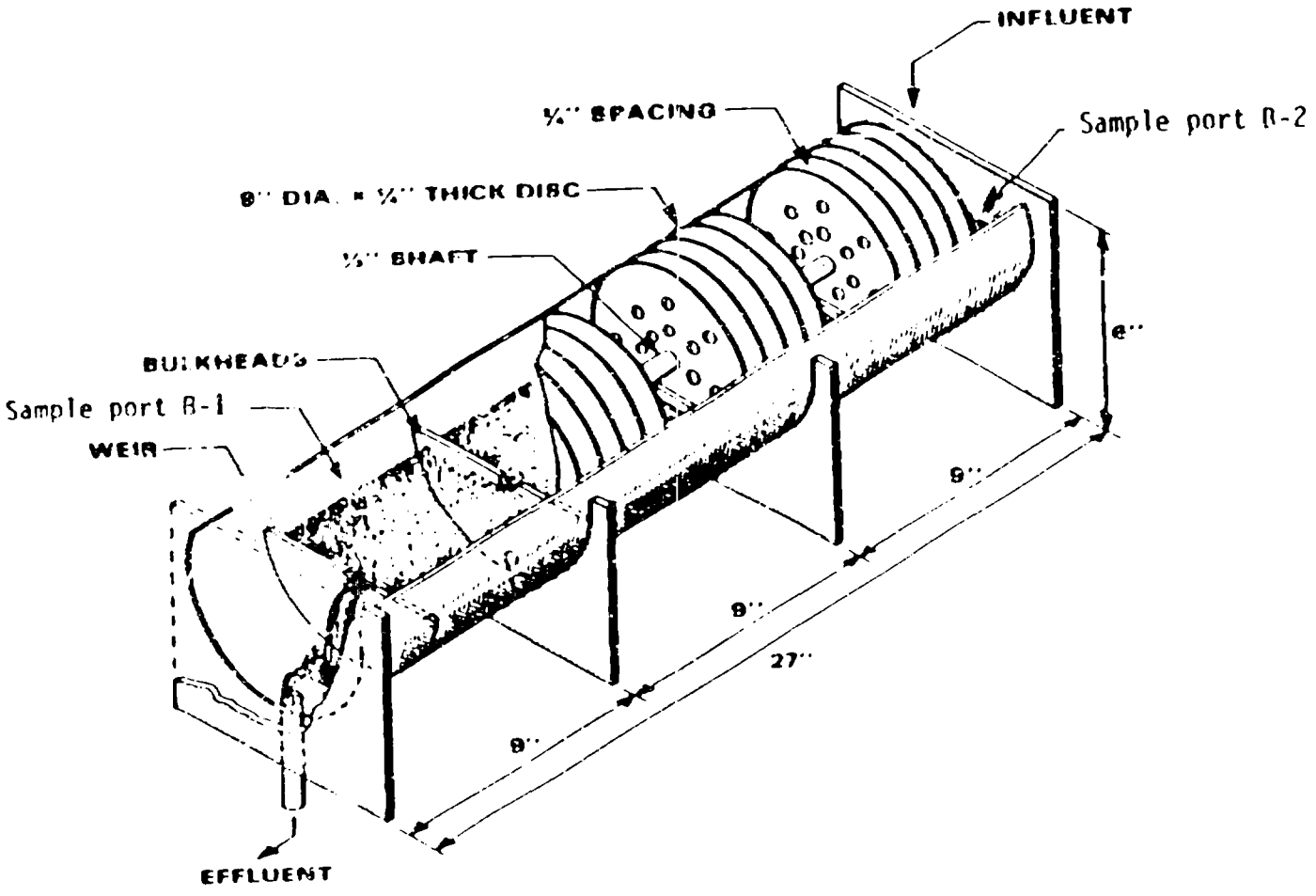


Figure 99. Bench scale rotating biological contactor (RBC)

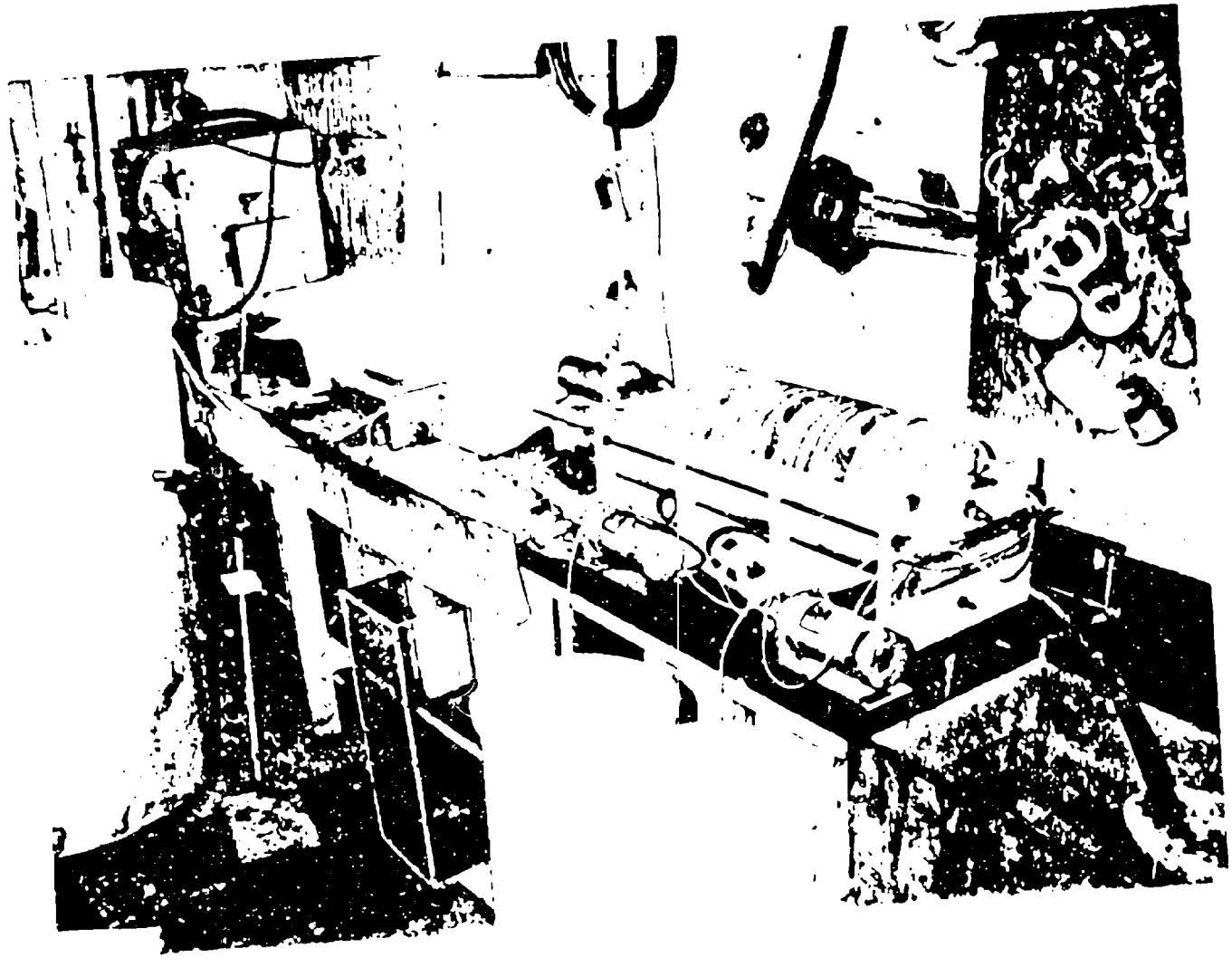


Figure 100. Bench-scale rotating biological contactor

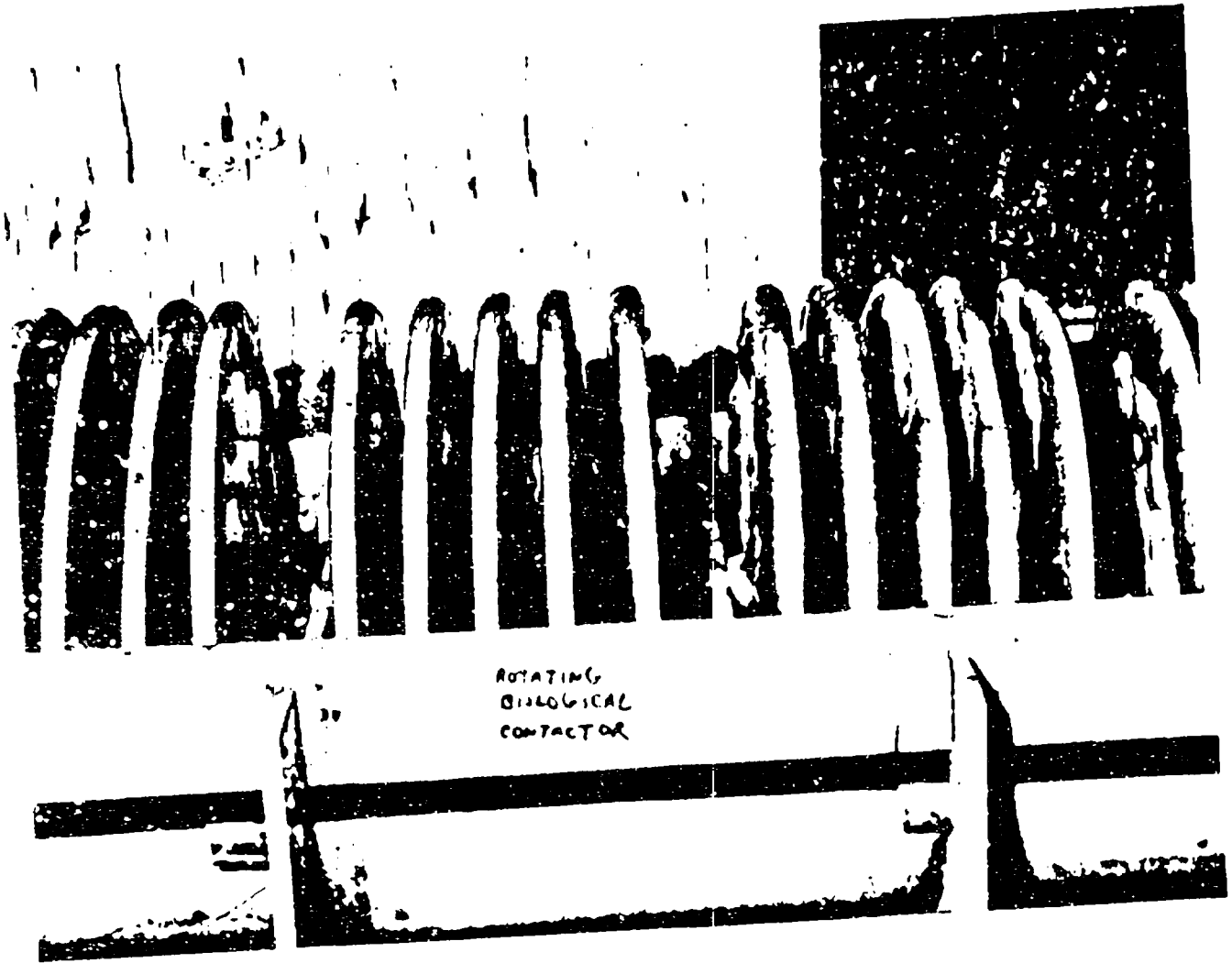
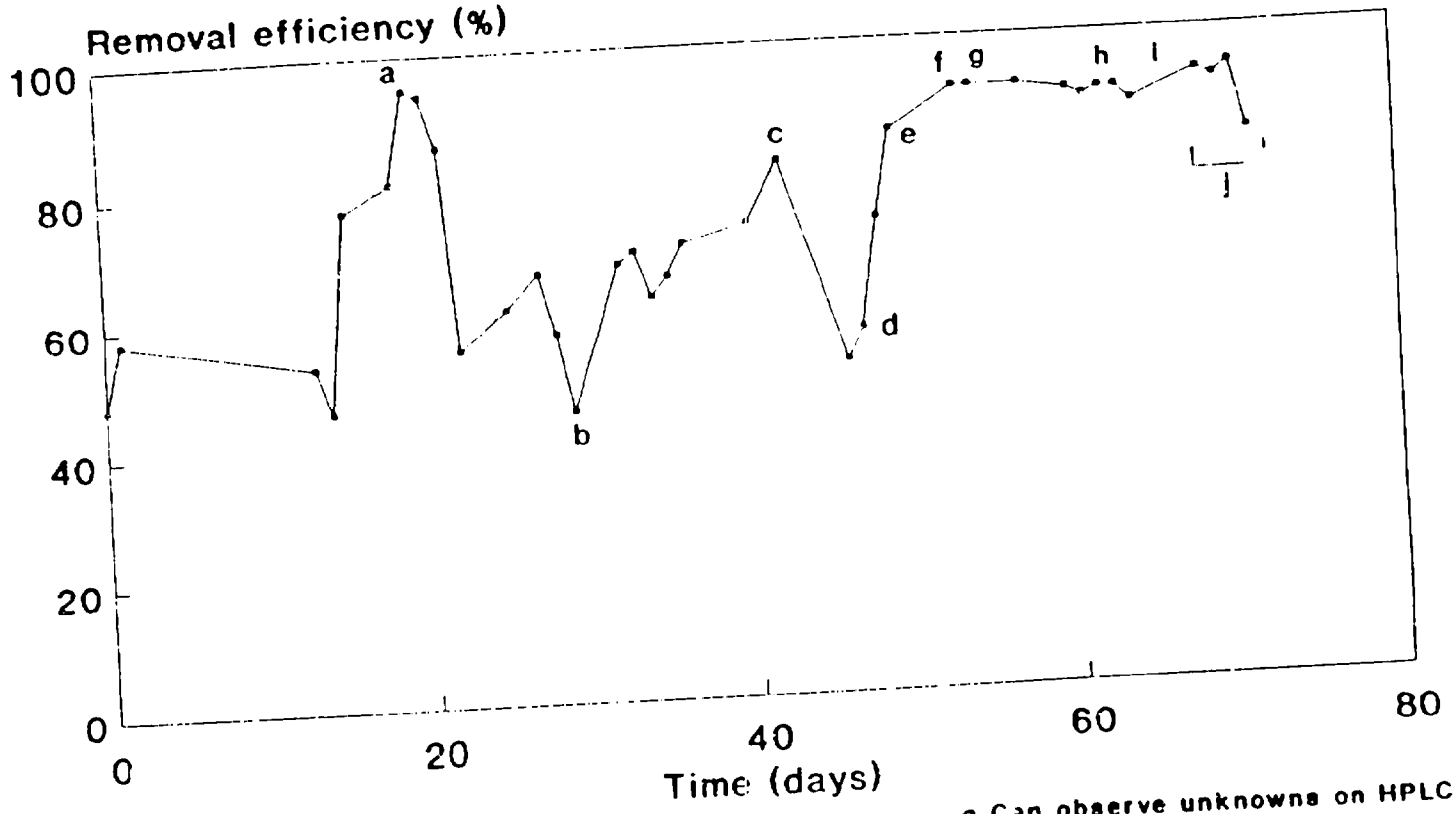


Figure 101. Close-up photograph of microorganisms on contactors

Figure 102. Rotating biological contactor effluent collector

Figure 103

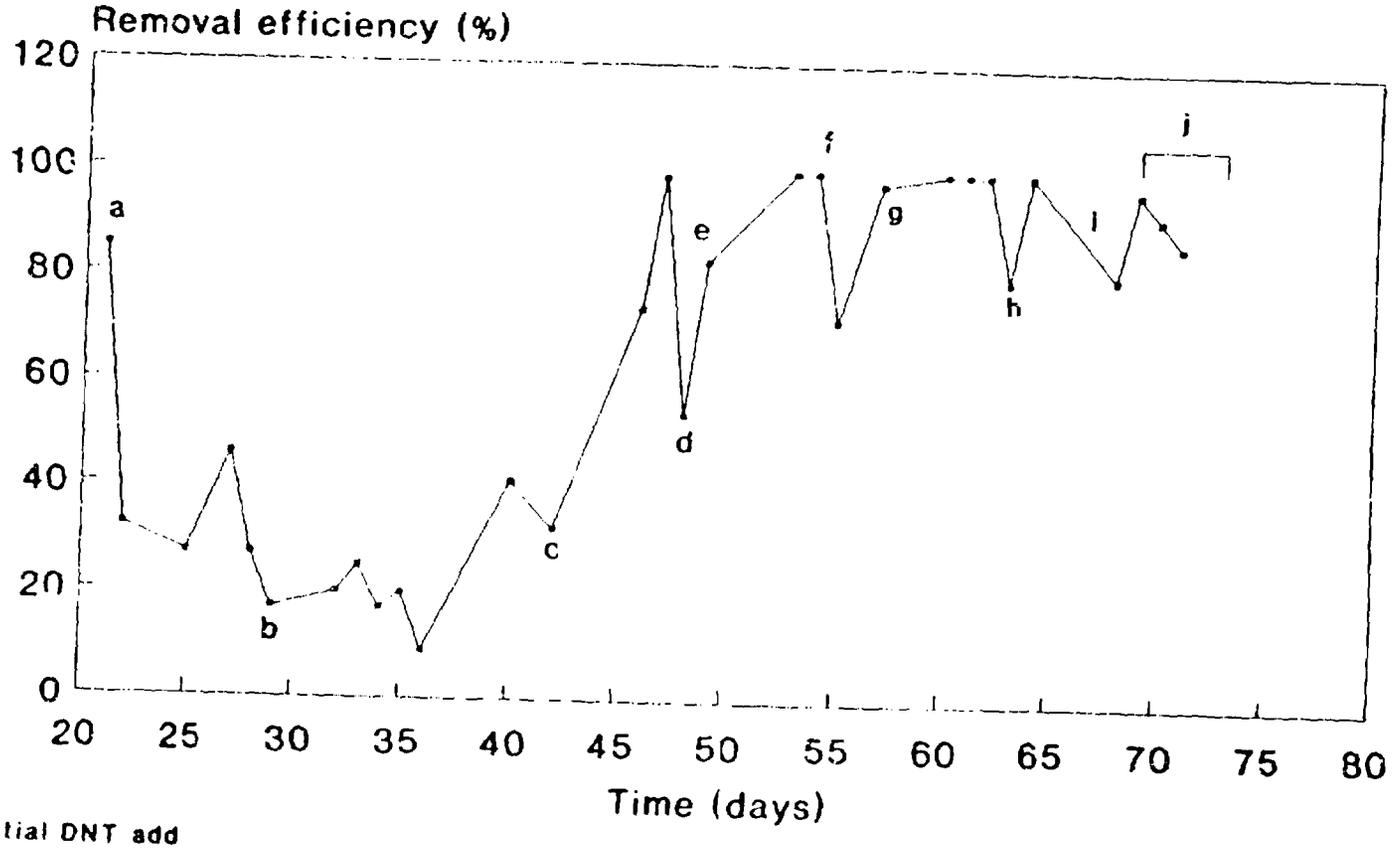
COD REMOVAL EFFICIENCY



a Initial DNT add
b Reseeded RBC with bioplant sludge
c Decreased flow rate (50%)
d Feed concentration increased
e Power shutdown - anaerobic (4 hours)
f Flow rate increased (66% of original)

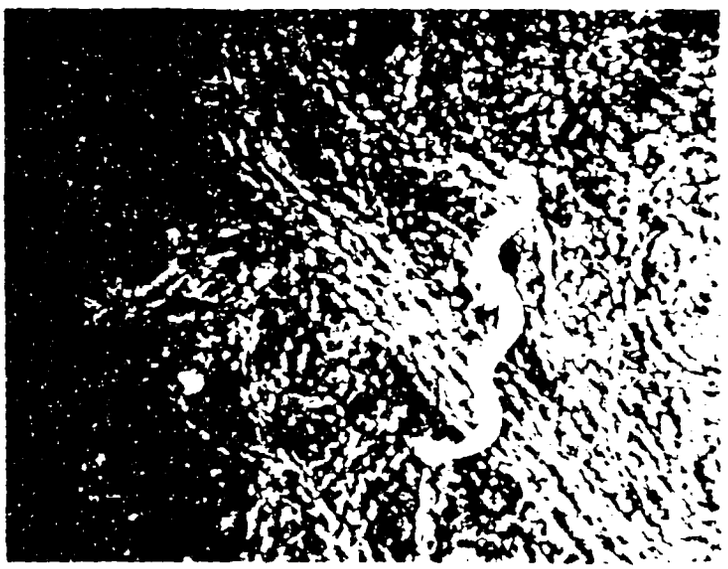
g Can observe unknowns on HPLC
h Increased flow rate to 75 mL/min
i System failure over weekend (no flow for several days)
j Influent DNT concentration increased 100% (18.6 to 36.8 mg/L)

Figure 104
DNT REMOVAL EFFICIENCY



a Initial DNT add
b Reseeded RBC with bioplant sludge
c Decreased flow rate (60%)
d Feed concentration increased
e Power shutdown - anaerobic (4 hours)
f Flow rate increased (66% of original)
g Can observe unknowns on HPLC
h Increased flow rate to 75 mg/L
i System failure over weekend (no flow for several days)
j Influent DNT concentration increased 100% (18.6 to 36.8 mg/L)

Stage 1



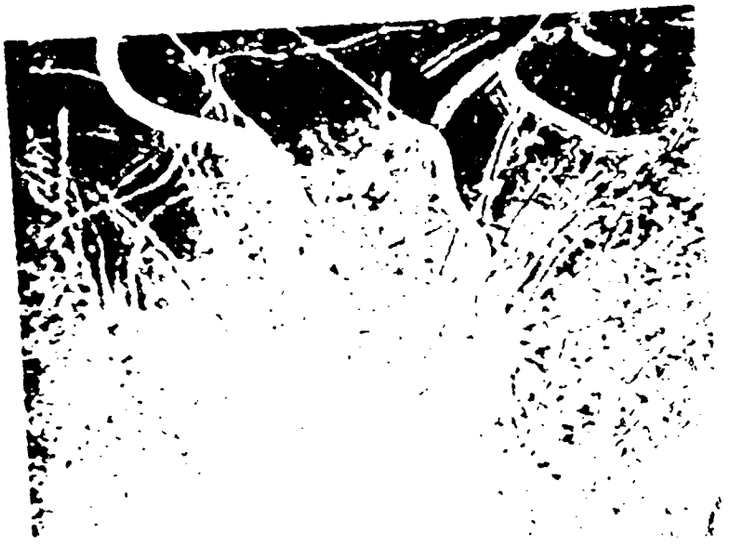
Stage 2

Figure 105. Biomass from bench-scale rotating biological contactor on da: 26

Stage 3

Stage 4

Figure 106. Biomass from bench-scale rotating biological contactor on day 26

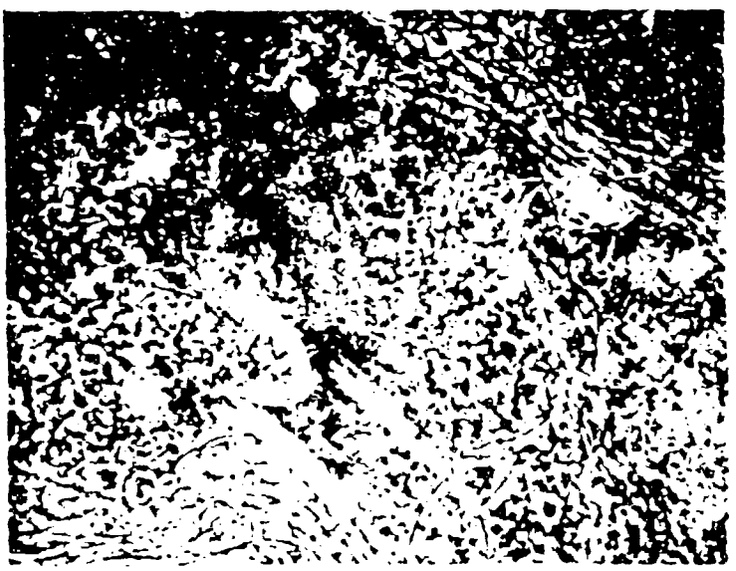


Stage 1

Stage 2

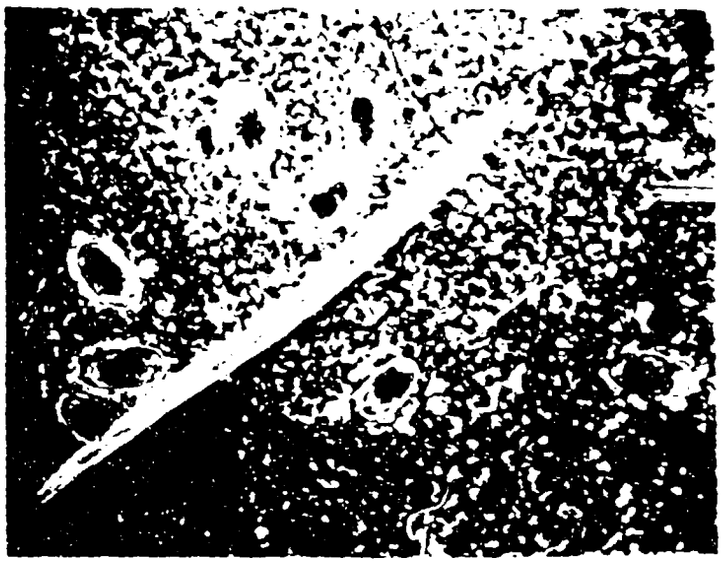
Figure 107. Biomass from bench-scale rotating biological contactor on day 35

Stage 3

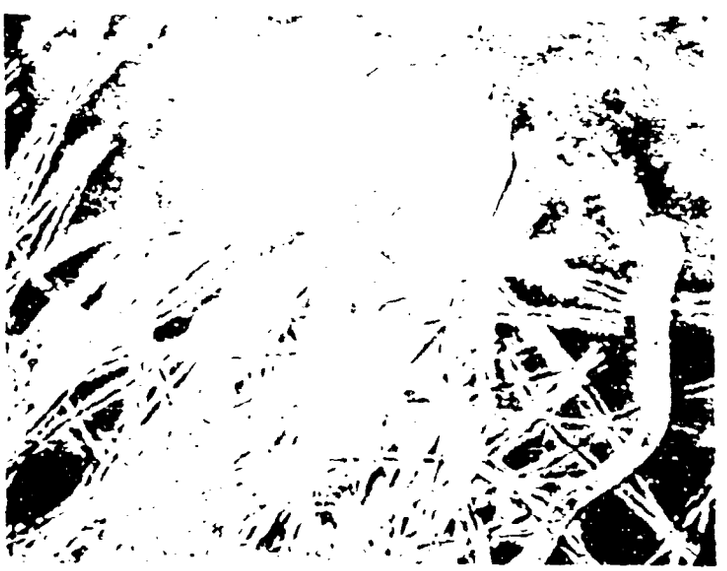


Stage 4

Figure 108. Biomass from bench-scale rotating biological contactor on day 35



Biomass



Fiber

Figure 109. Effluent collector

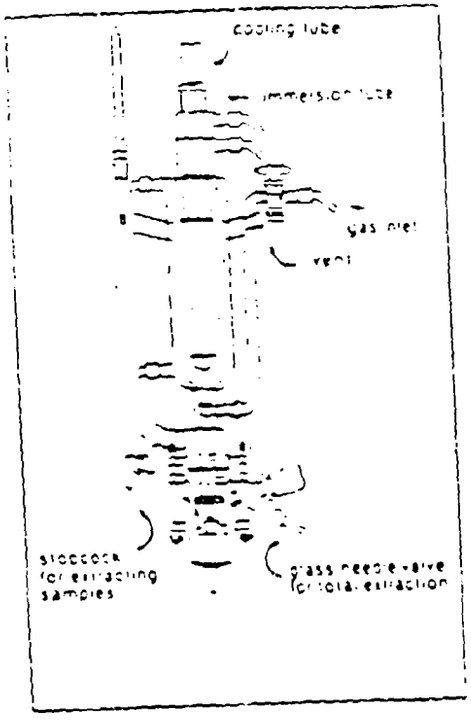


Figure 110. Normag photoreactor

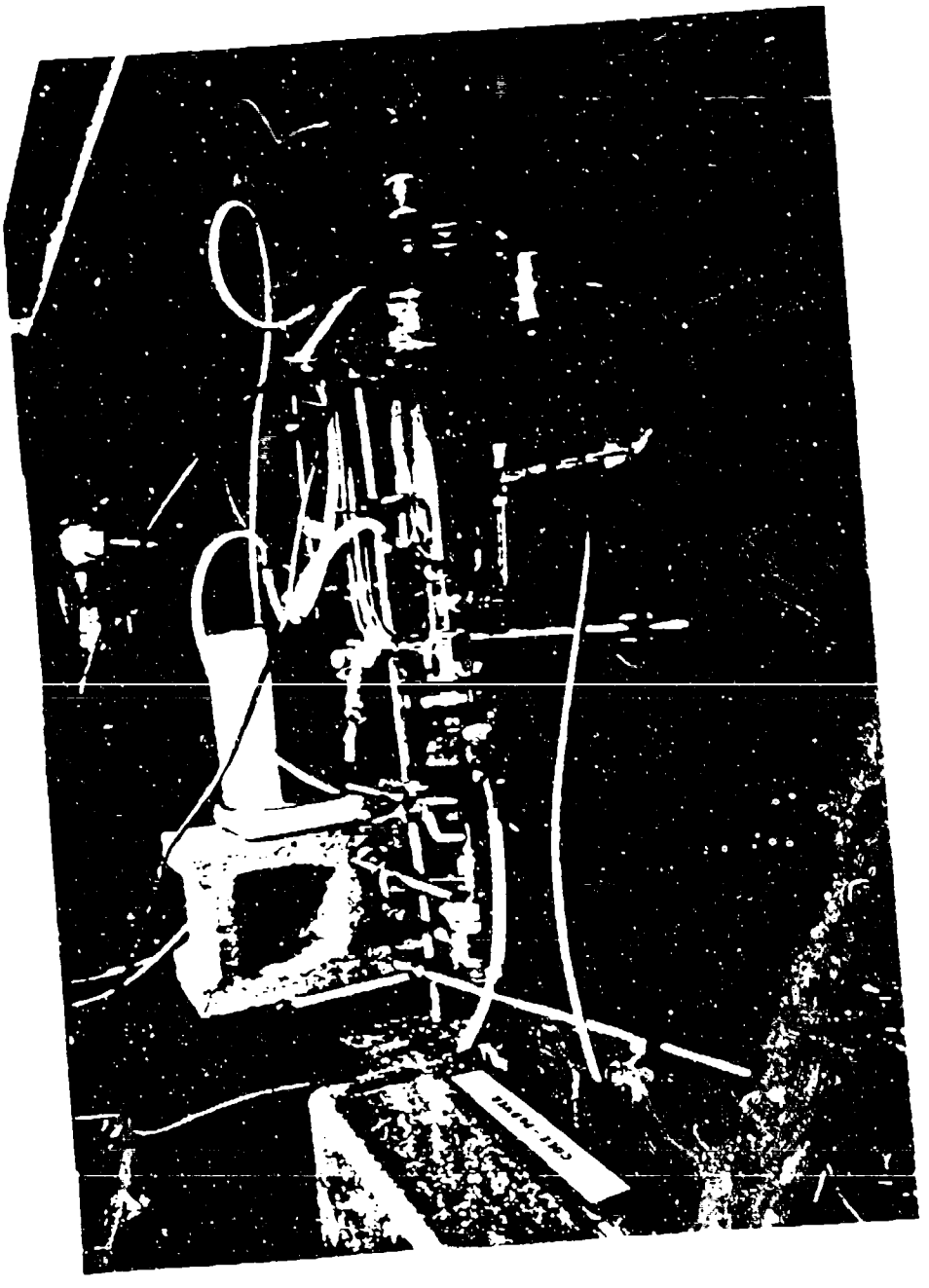


Figure 111. Bench-scale UV/ozone reactor

Figure 112. Ozone generator and power supplies for UV bulb

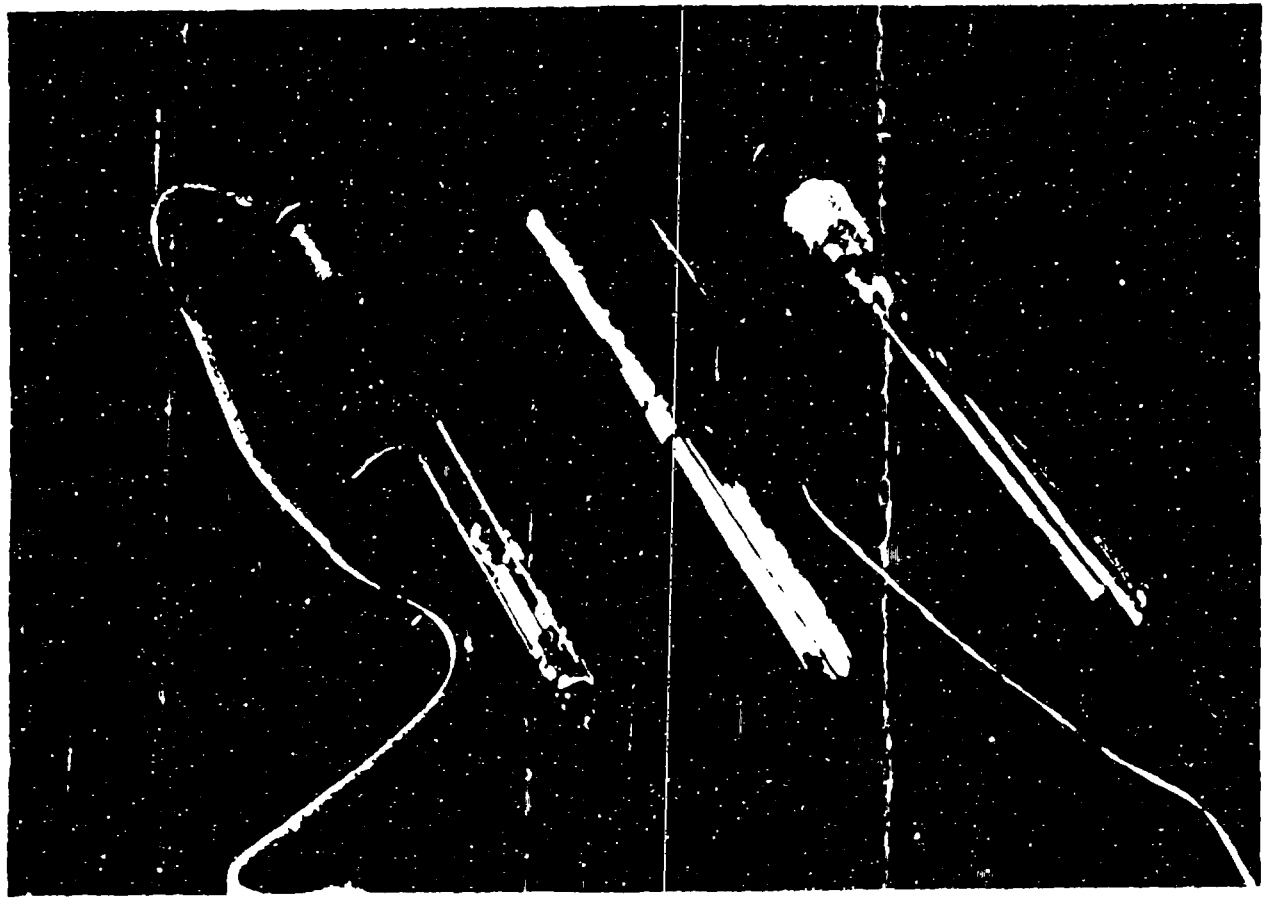


Figure 113. UV reactor bulbs and cooling jacket

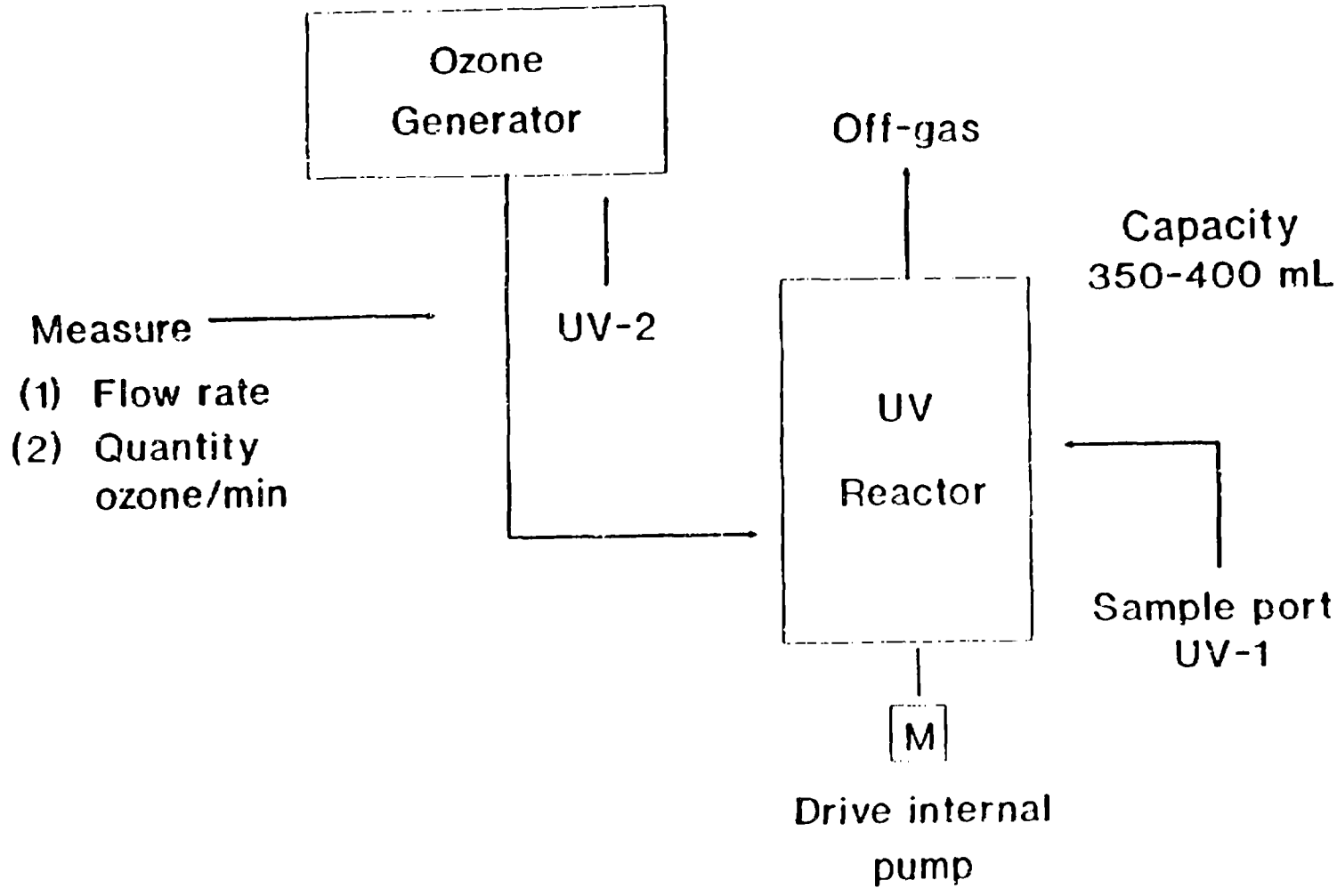


Figure 114. Flow diagram of UV/ozone reactor

Figure 115

EFFECT OF VARYING OZONE FLOW RATE OF REACTOR AT 254-NM

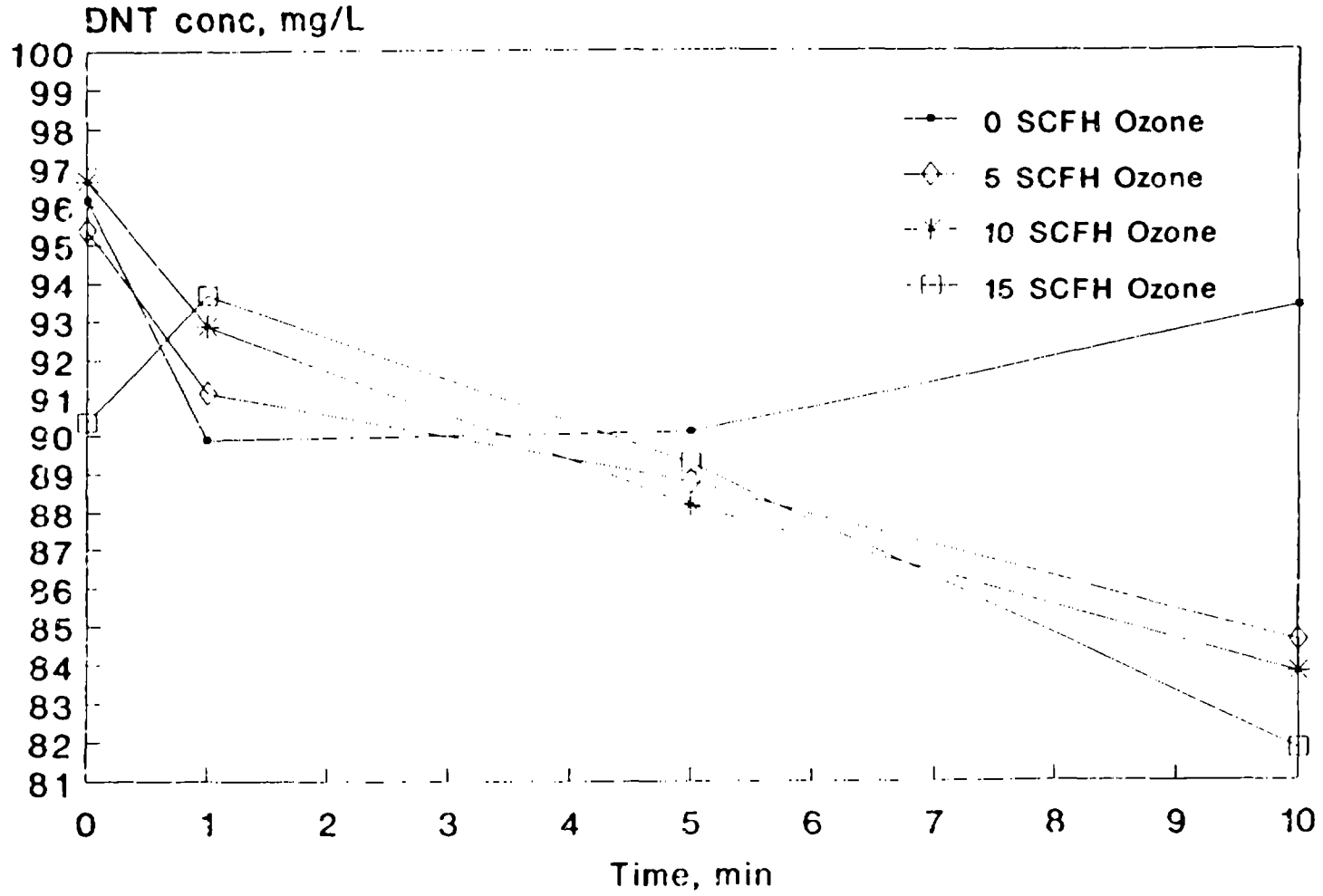


Figure 116

COMPARISON OF UV BULBS AT 10 SCFH

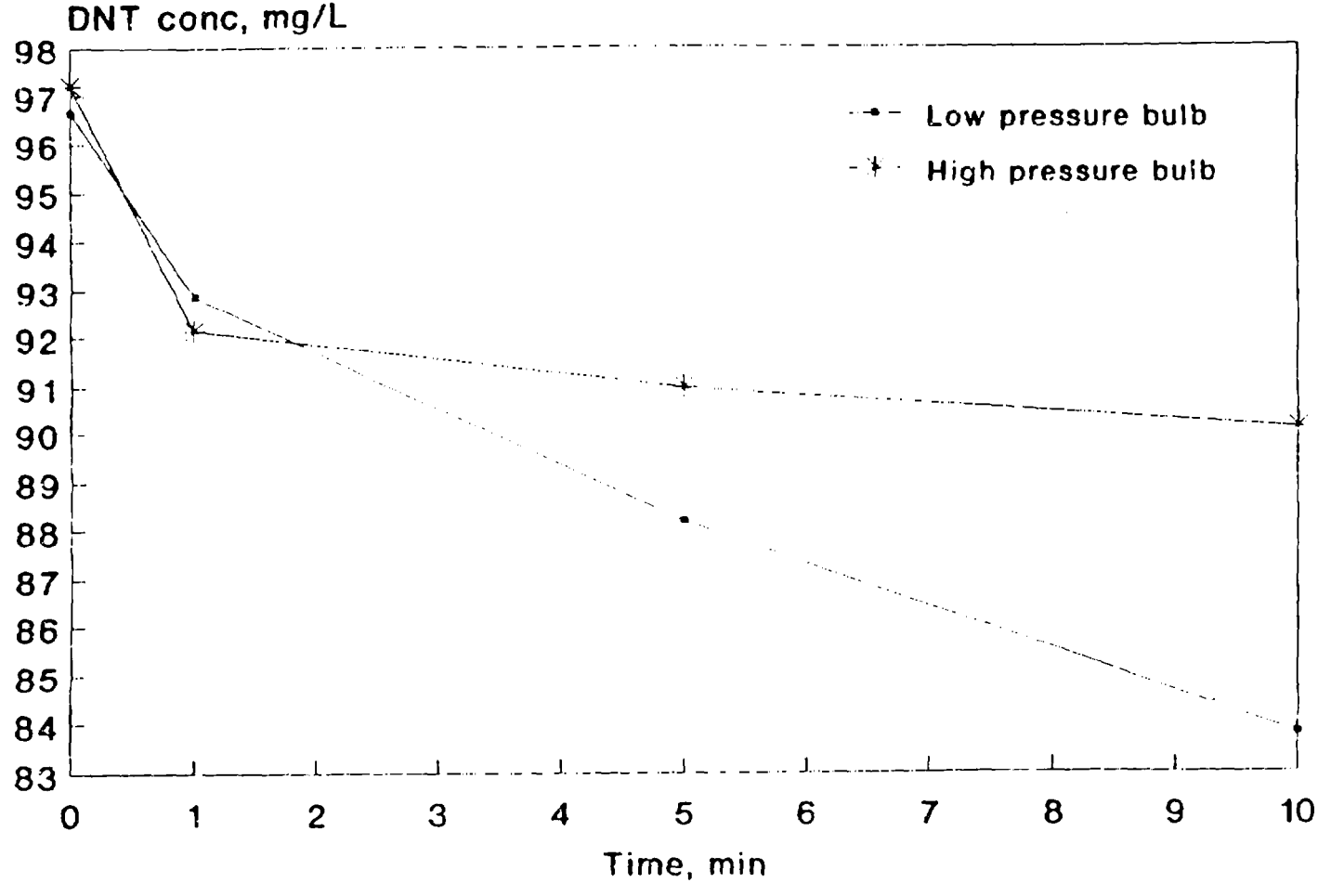


Figure 117

SOLVENT EFFECT AT OZONE FLOW RATE OF 5 SCFH AT 254-NM

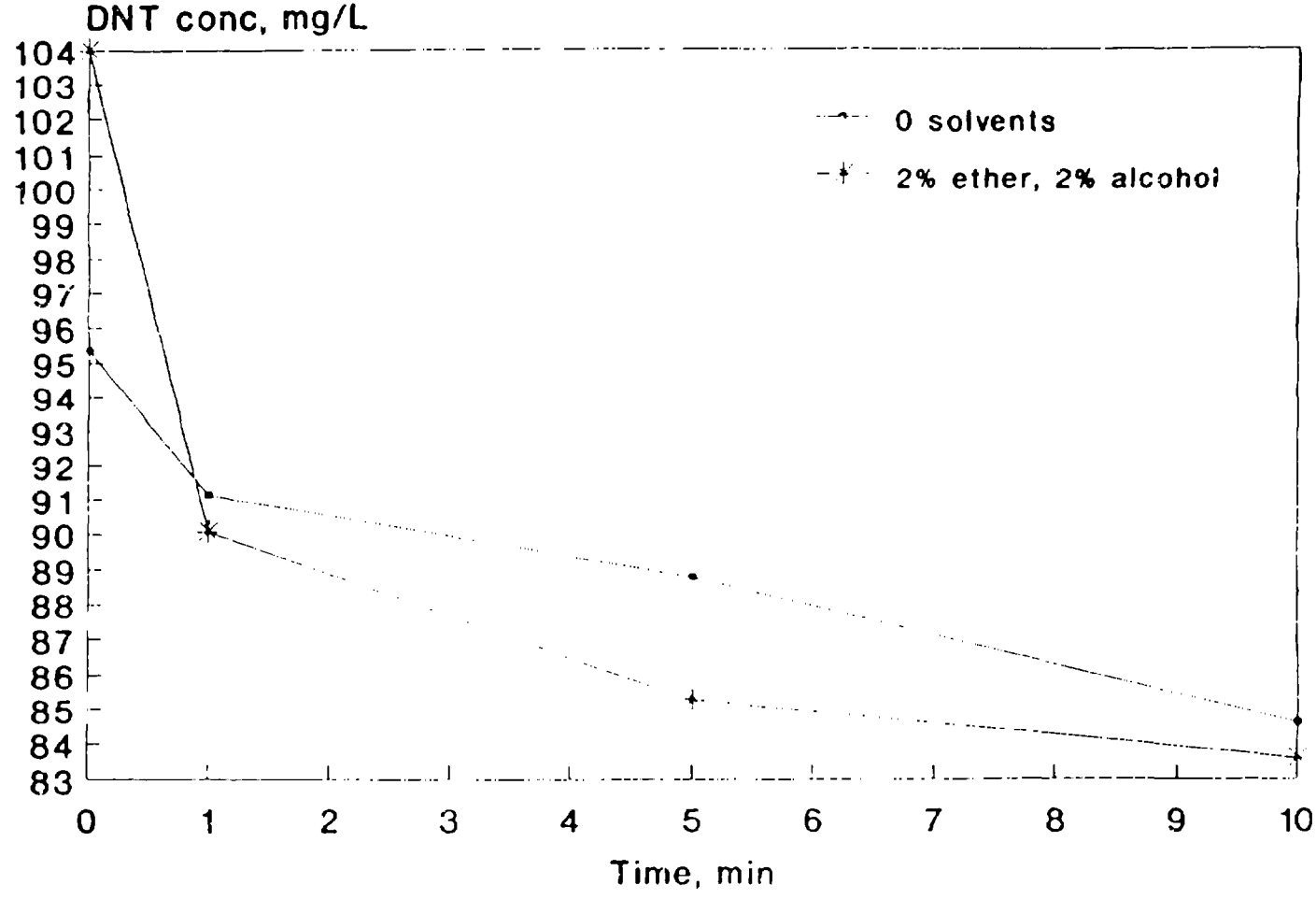


Figure 118

SOLVENT EFFECT AT OZONE FLOW RATE OF 10 SCFH AT 254-NM

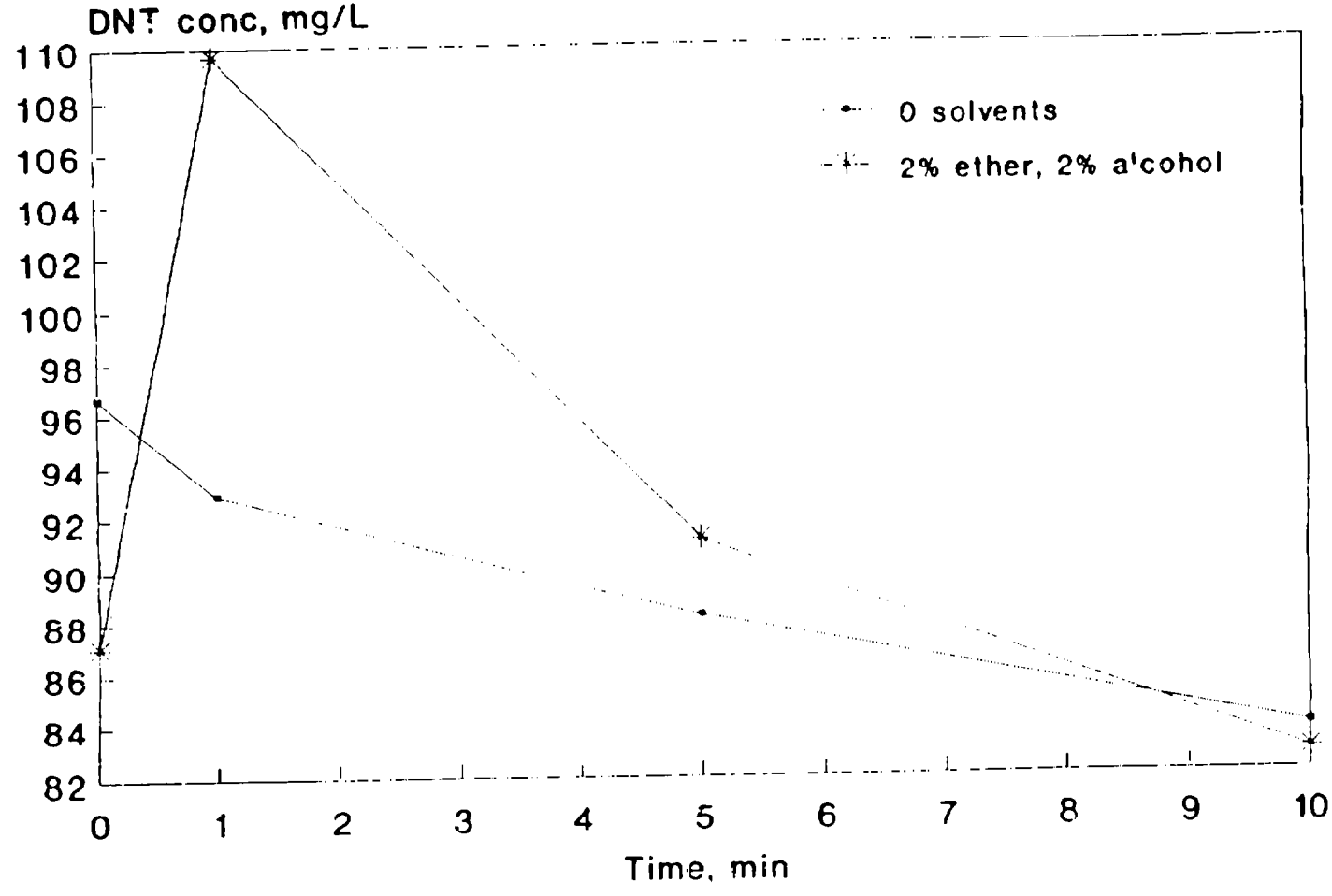


Figure 119

IRRADIATION OF STANDARD AT 254-NM

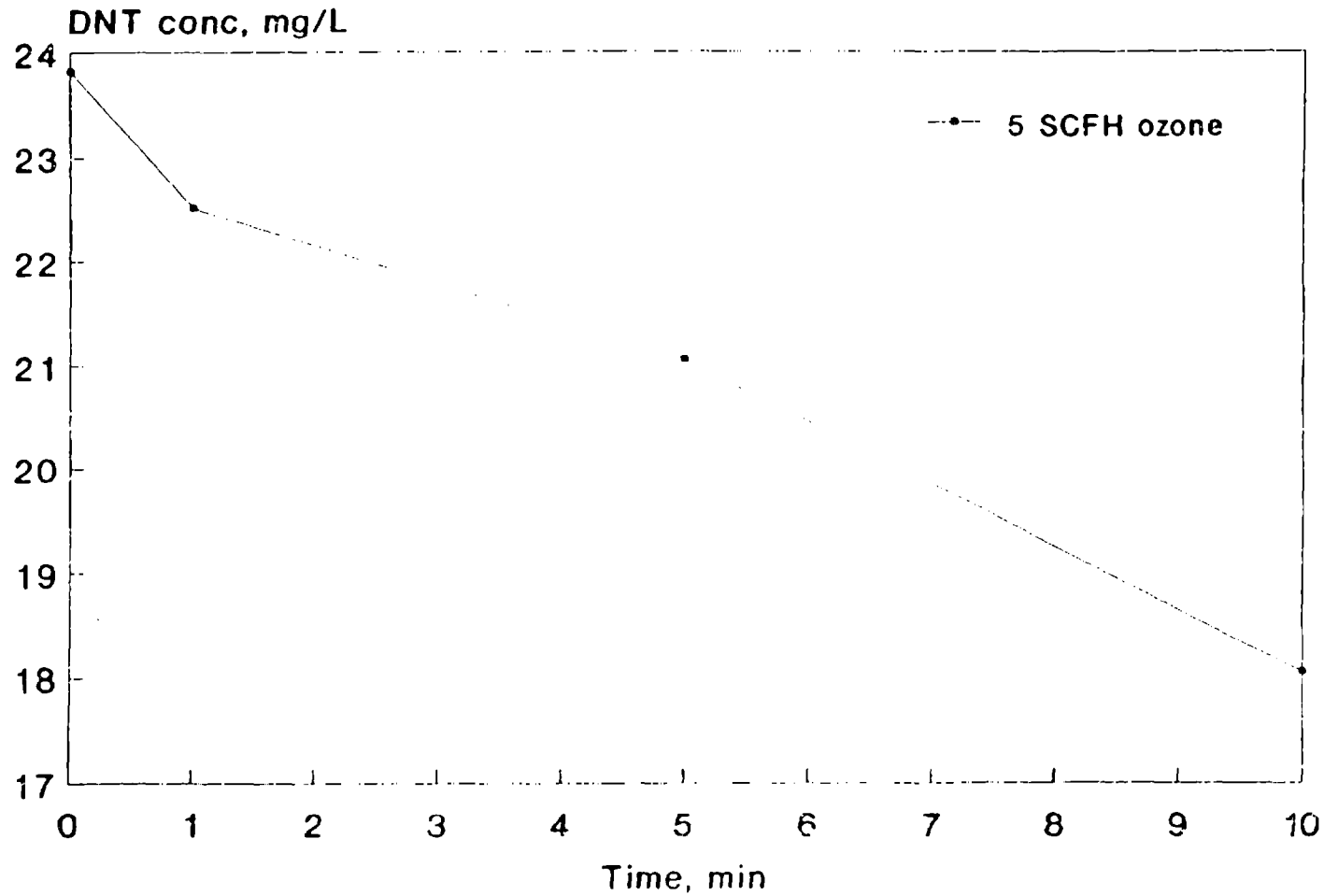


Figure 120

PRELIMINARY WASTEWATER IRRADIATED AT 254-NM

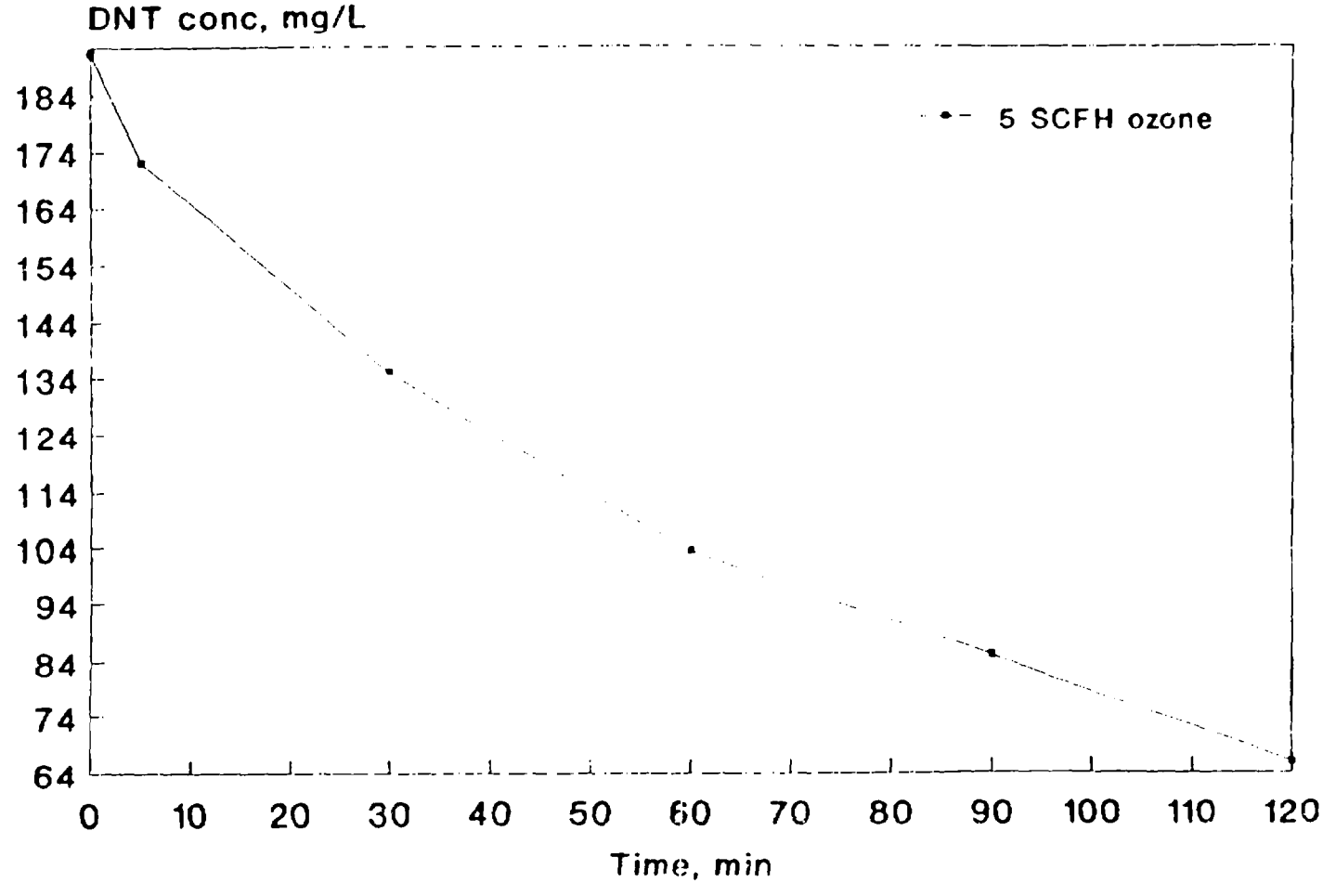


Figure 121

EFFECT OF VARYING OZONE FLOW RATE ON WASTEWATER AT 254-NM

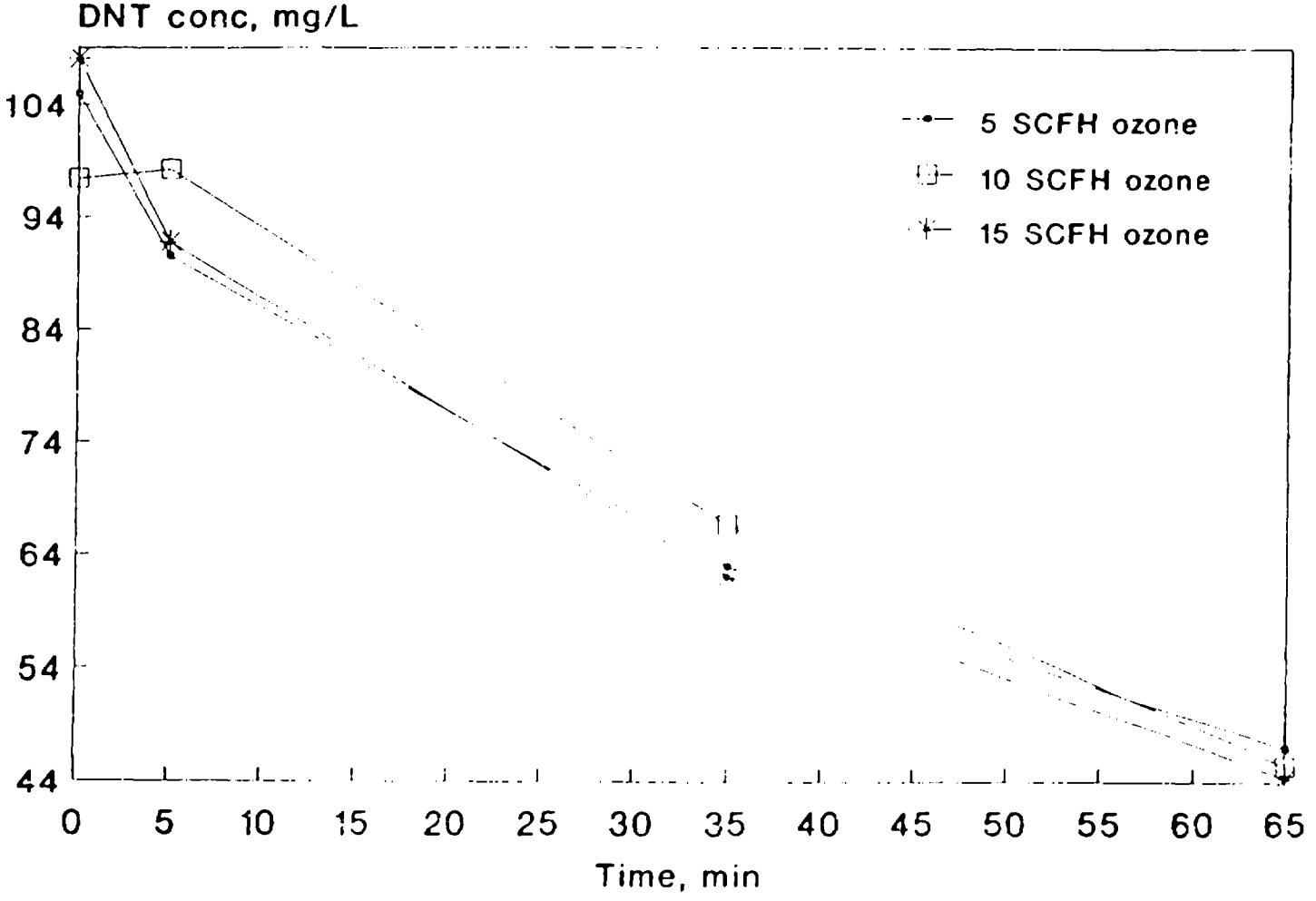


Figure 122

FINAL WASTEWATER EXPERIMENTS AT 254-NM

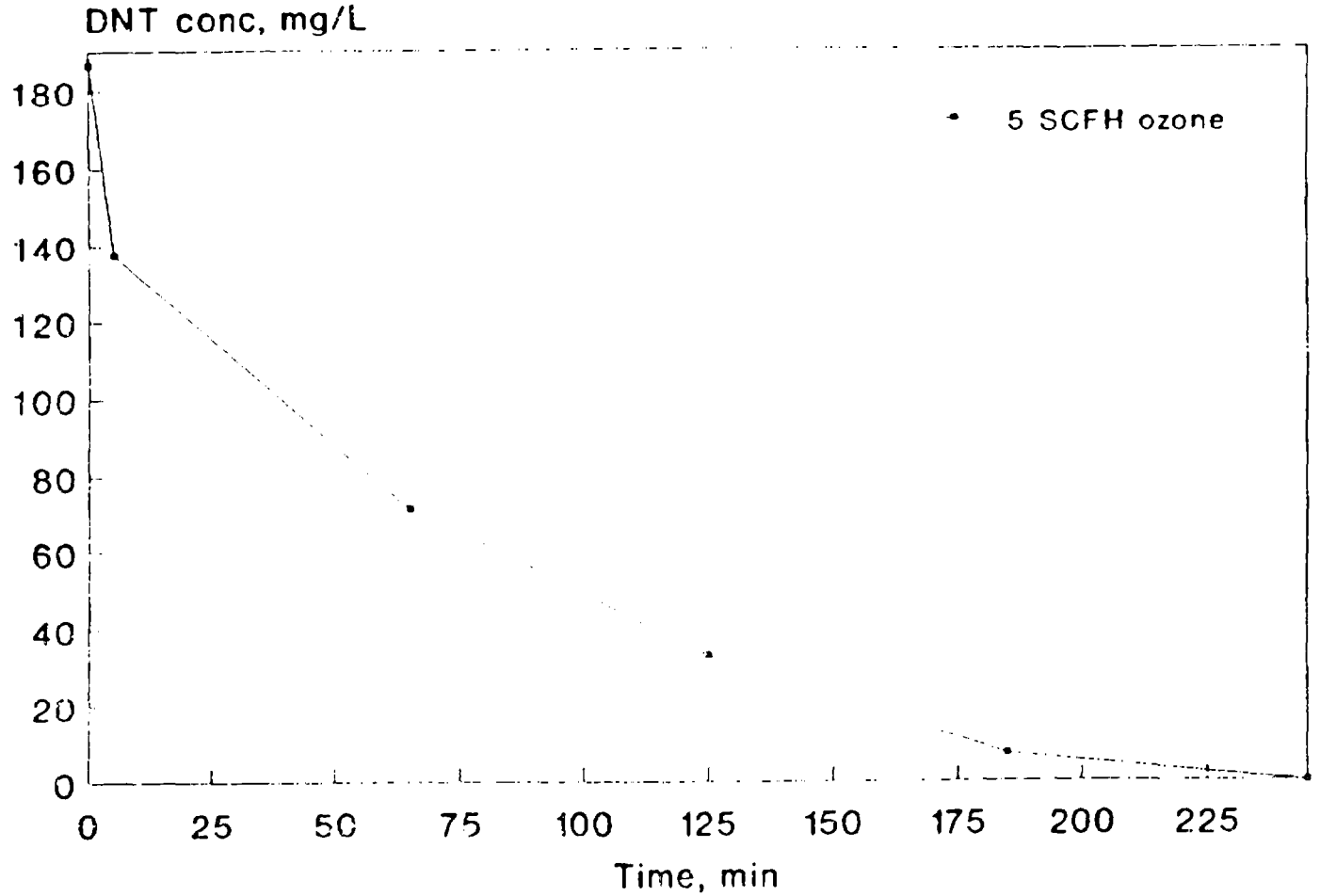
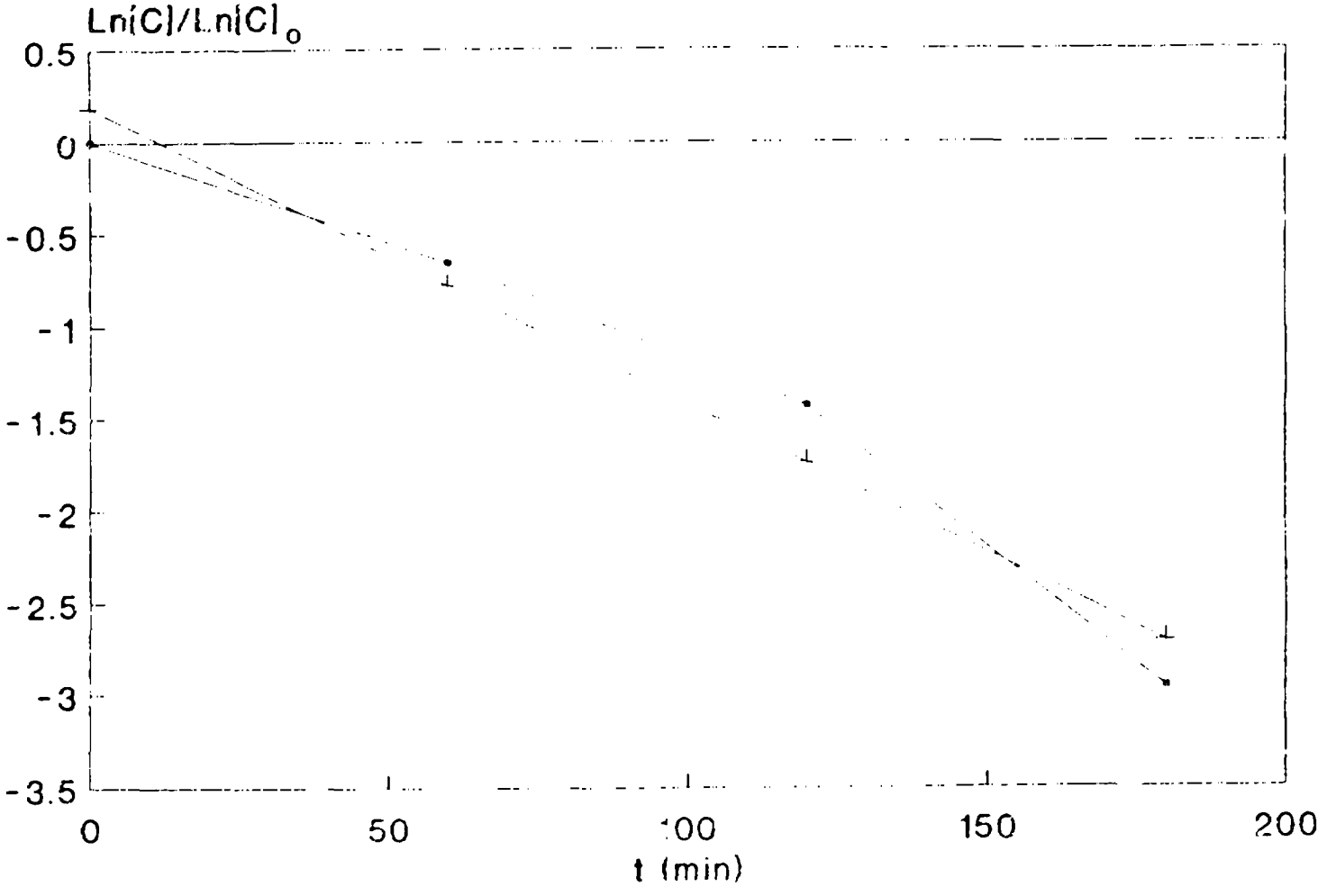


Figure 123

FIRST ORDER PLOT OF UV/OZONE DESTRUCTION OF DNT IN WASTEWATER



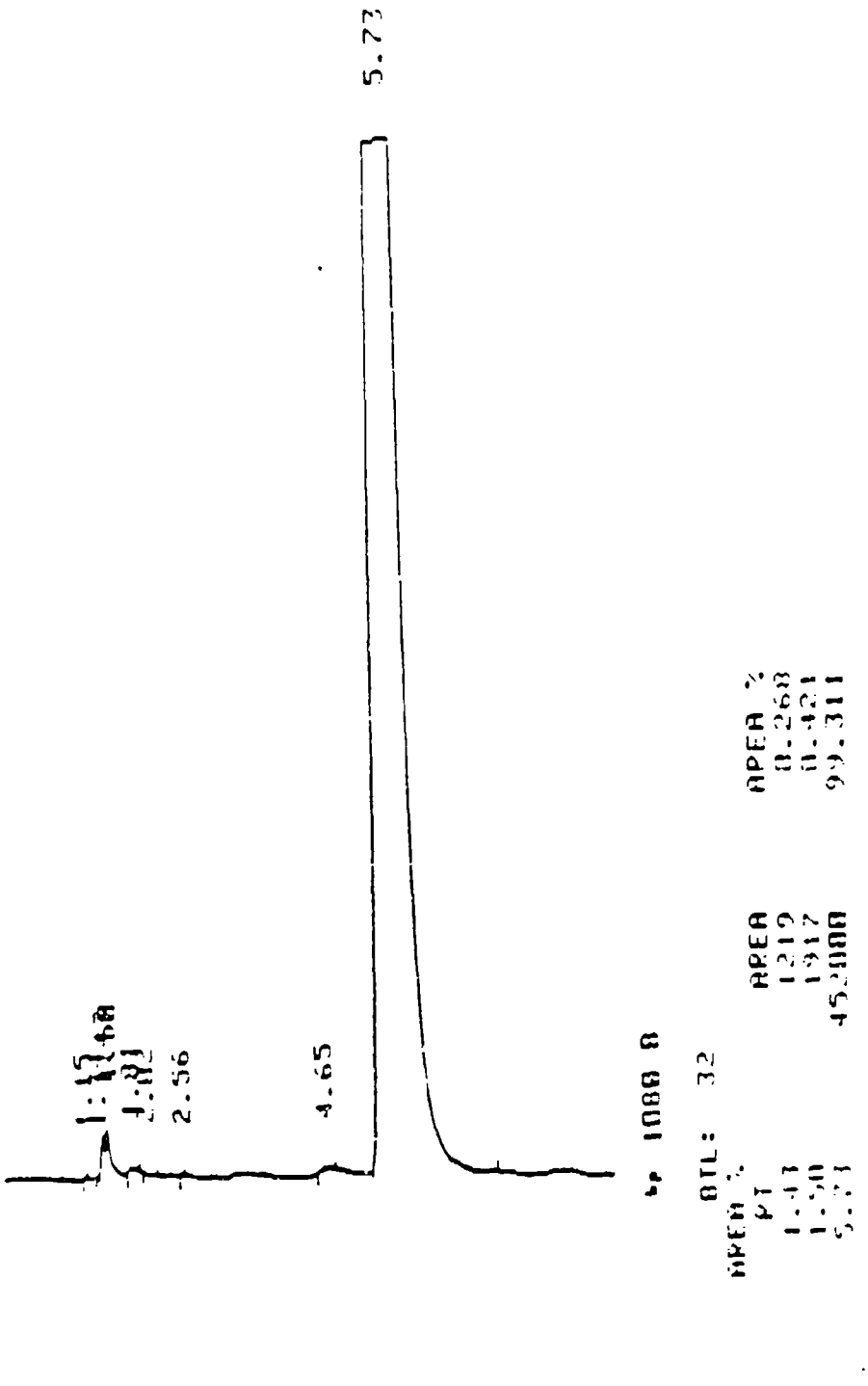


Figure 124. UV/ozone chromatogram of test 29 at 0 min

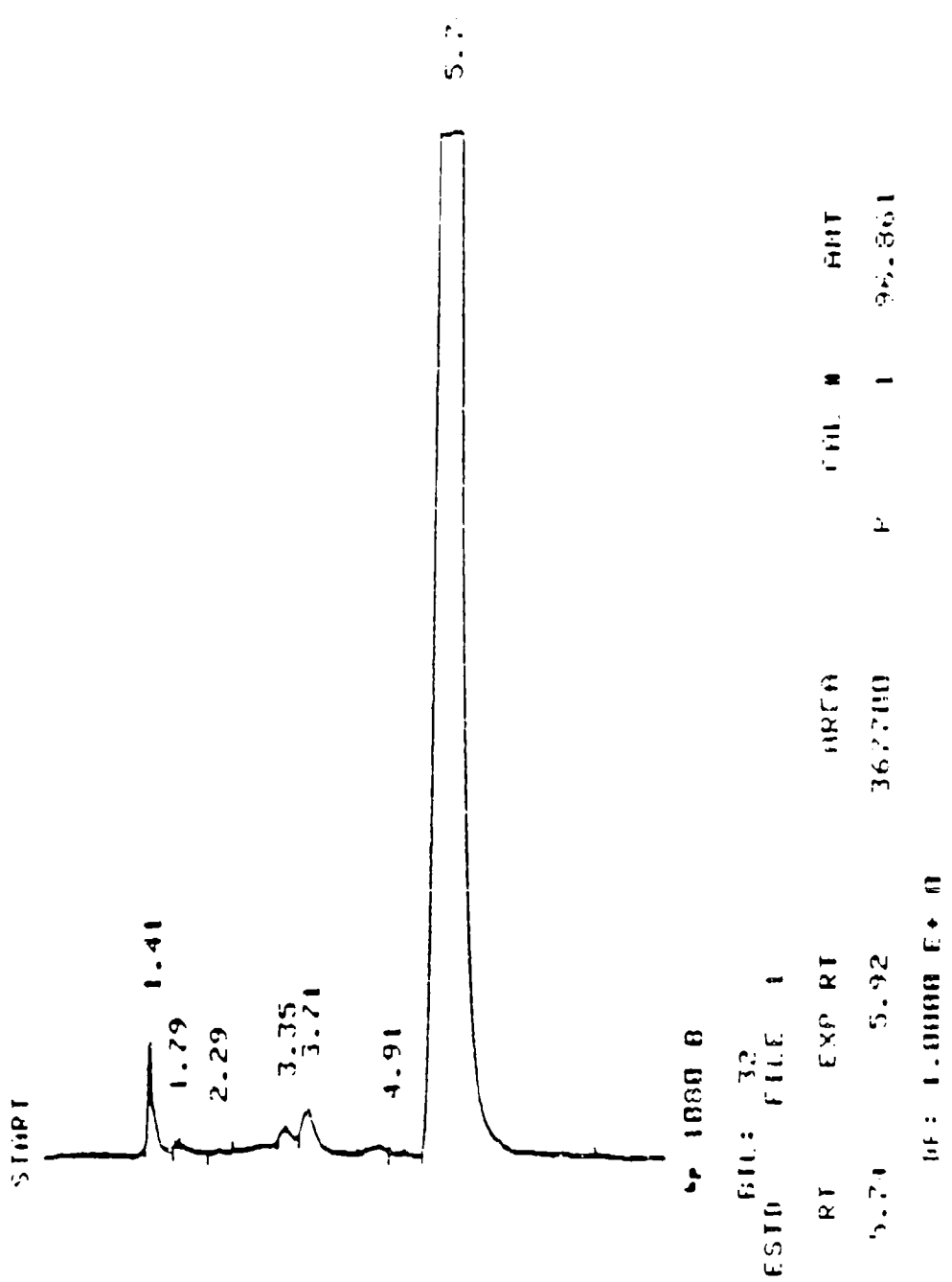


Figure 125. UV/ozone chromatogram of test 29 at 5 min

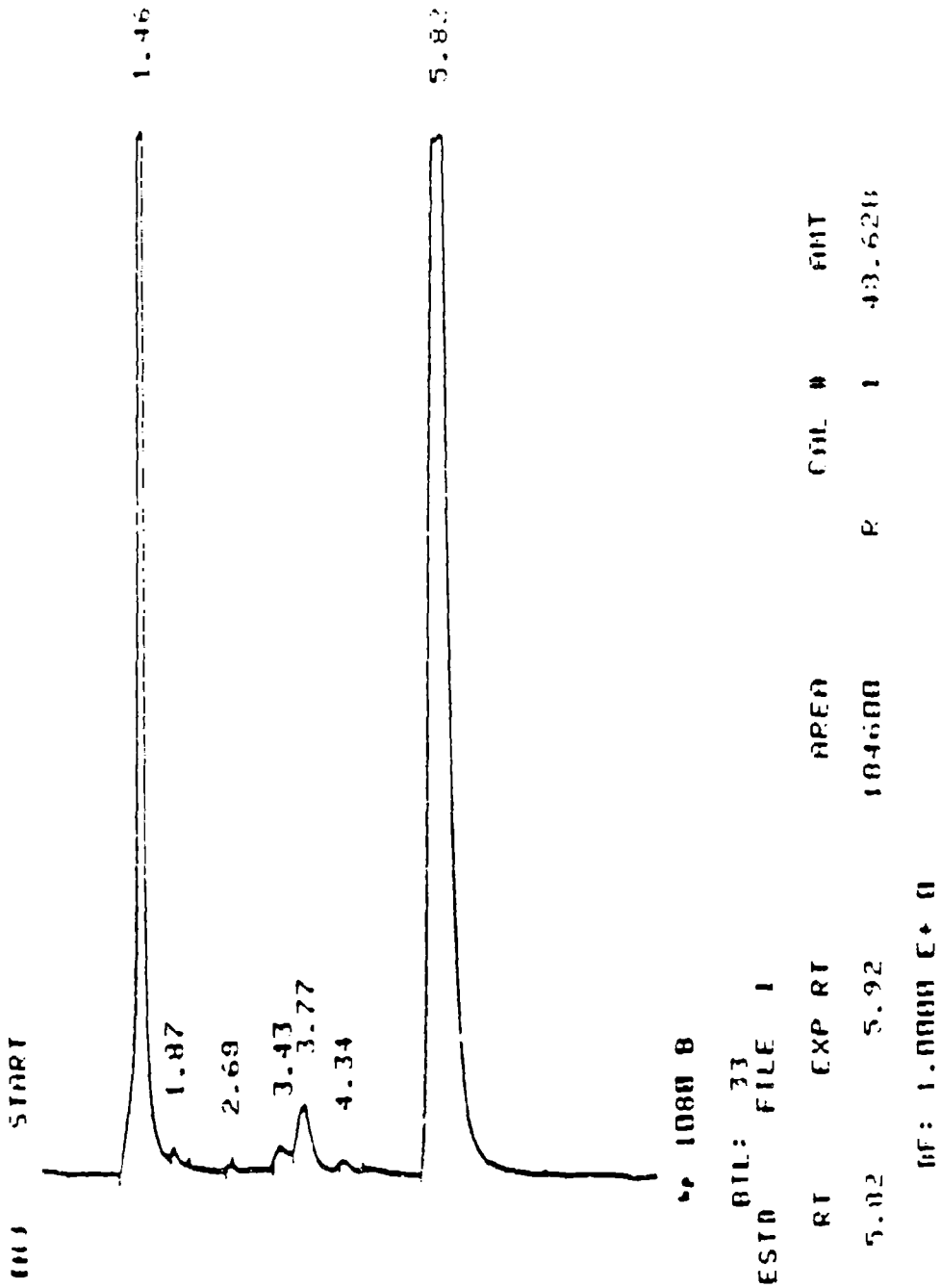


Figure 126. UV/ozone chromatogram of test 29 at 65 min

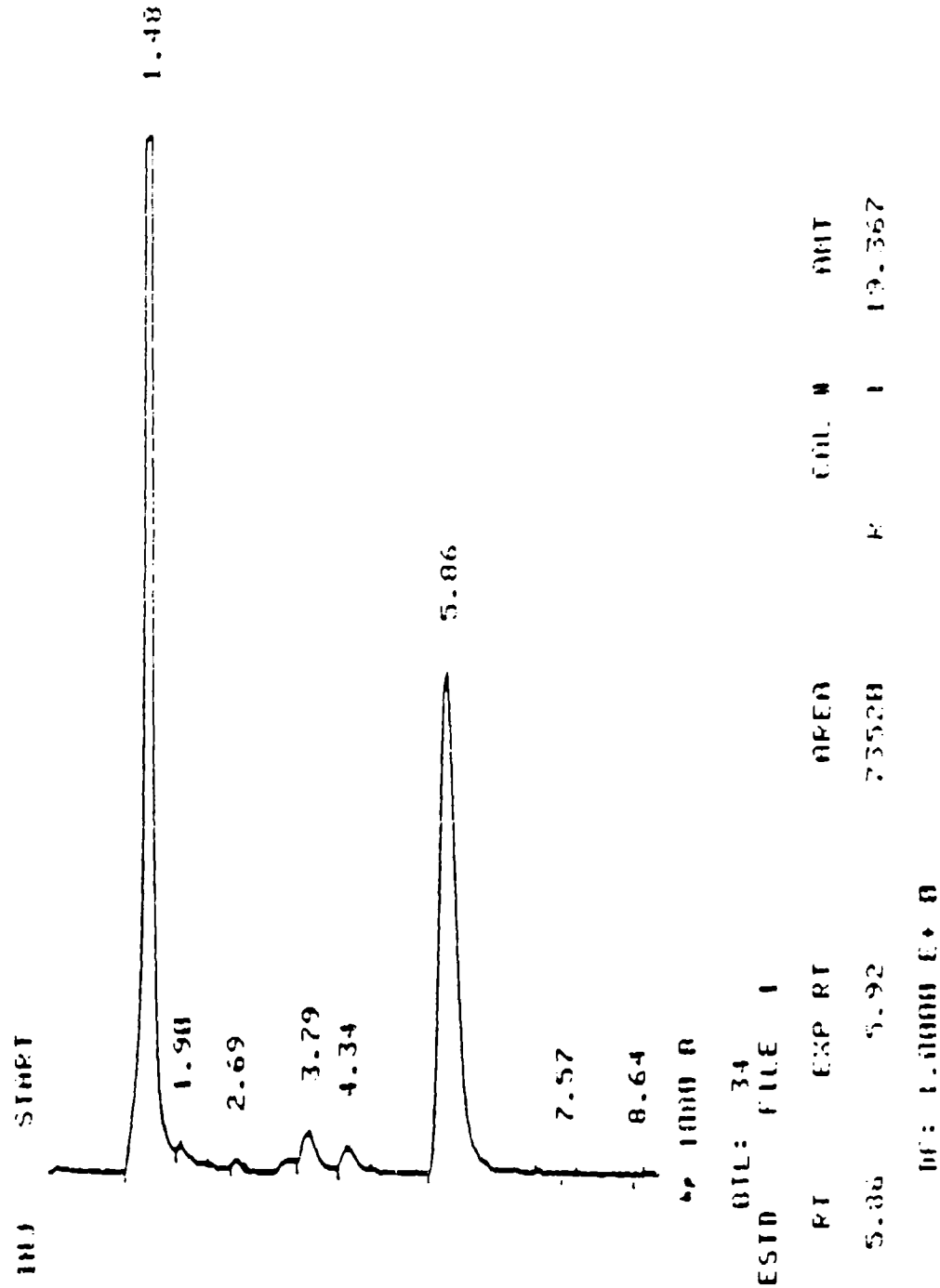


Figure 127. UV/ozone chromatogram of test 29 at 125 min

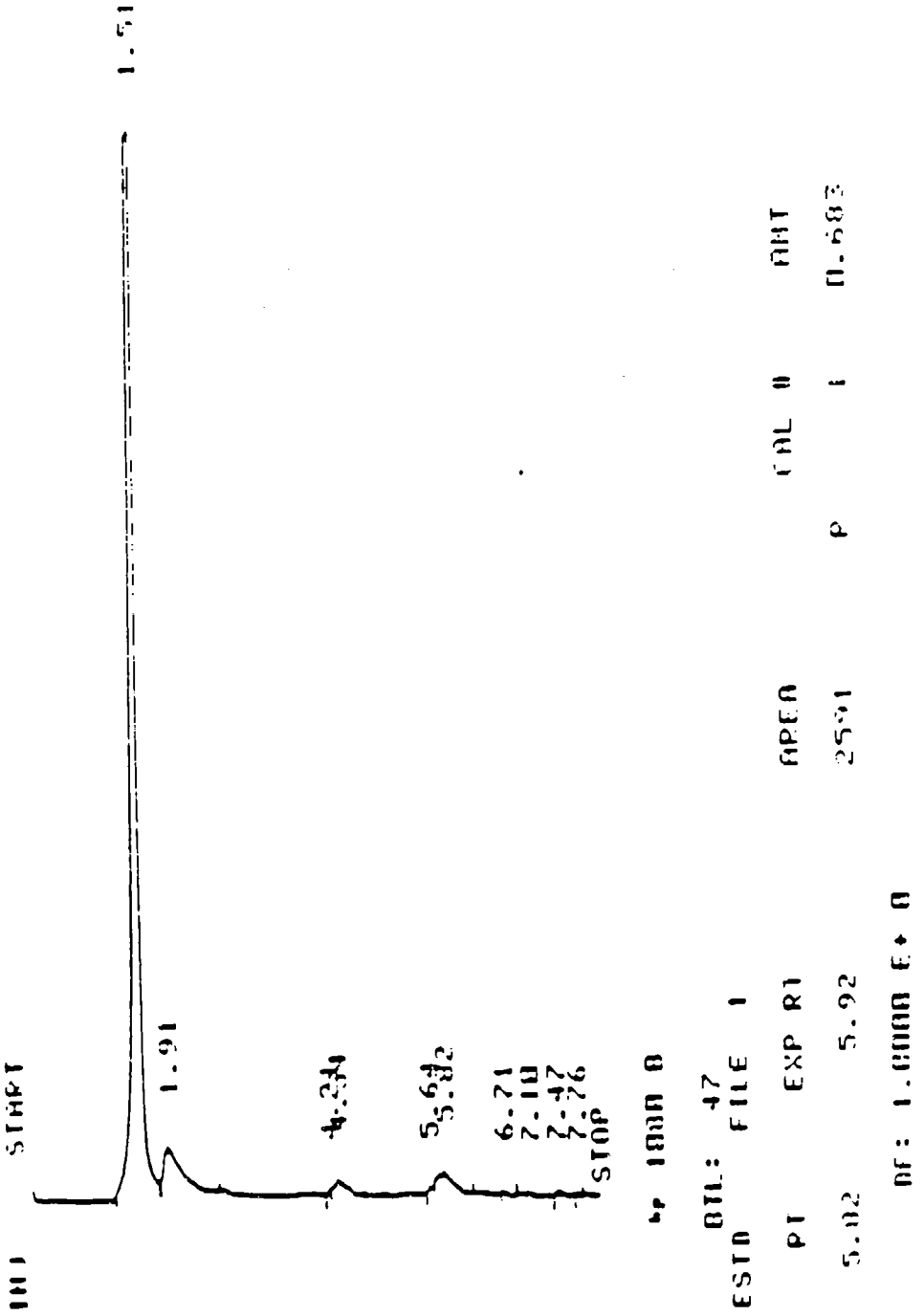


Figure 128. UV/ozone chromatogram of test 29 at 185 min

Figure 129. UV/ozone chromatogram of test 29 at 245 min

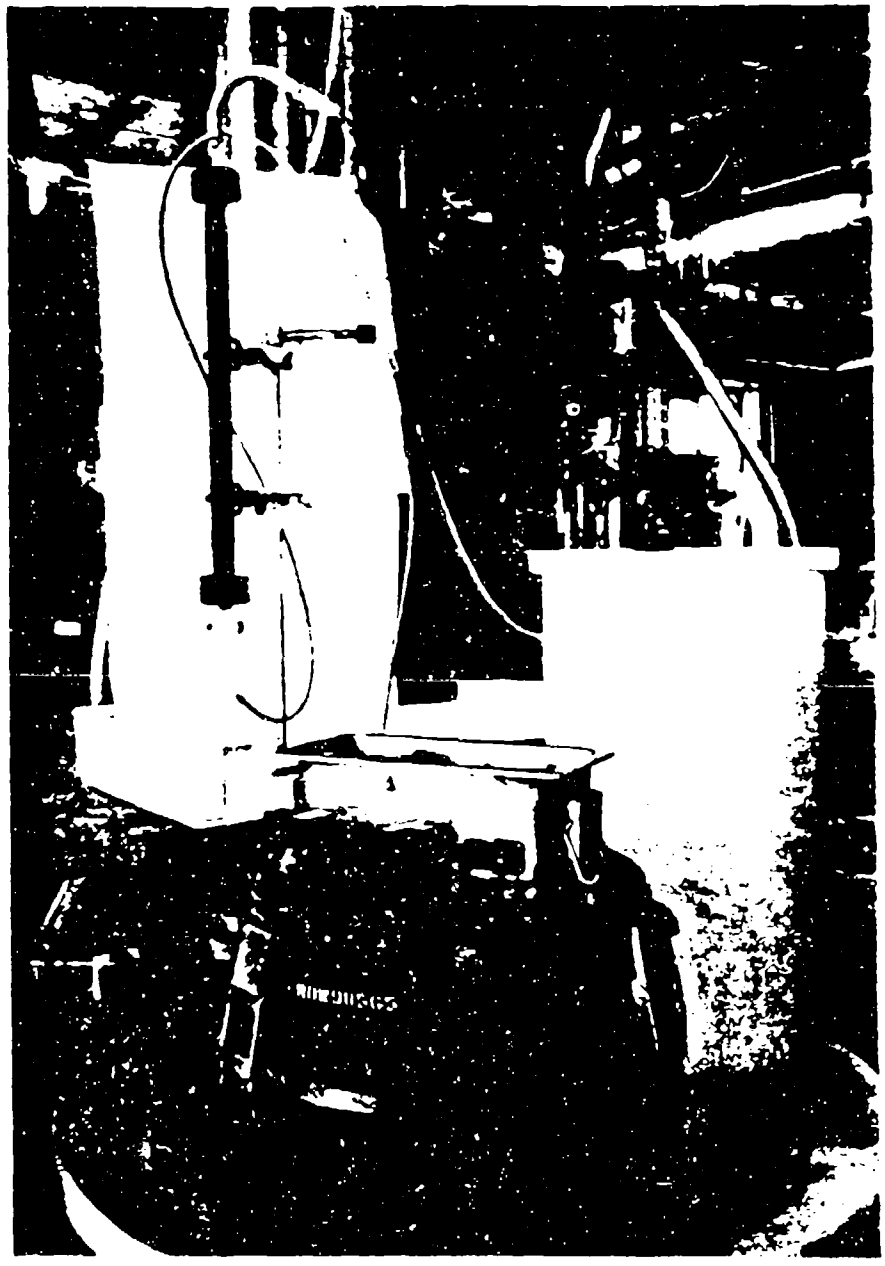


Figure 130. Bench-scale granular activated carbon column

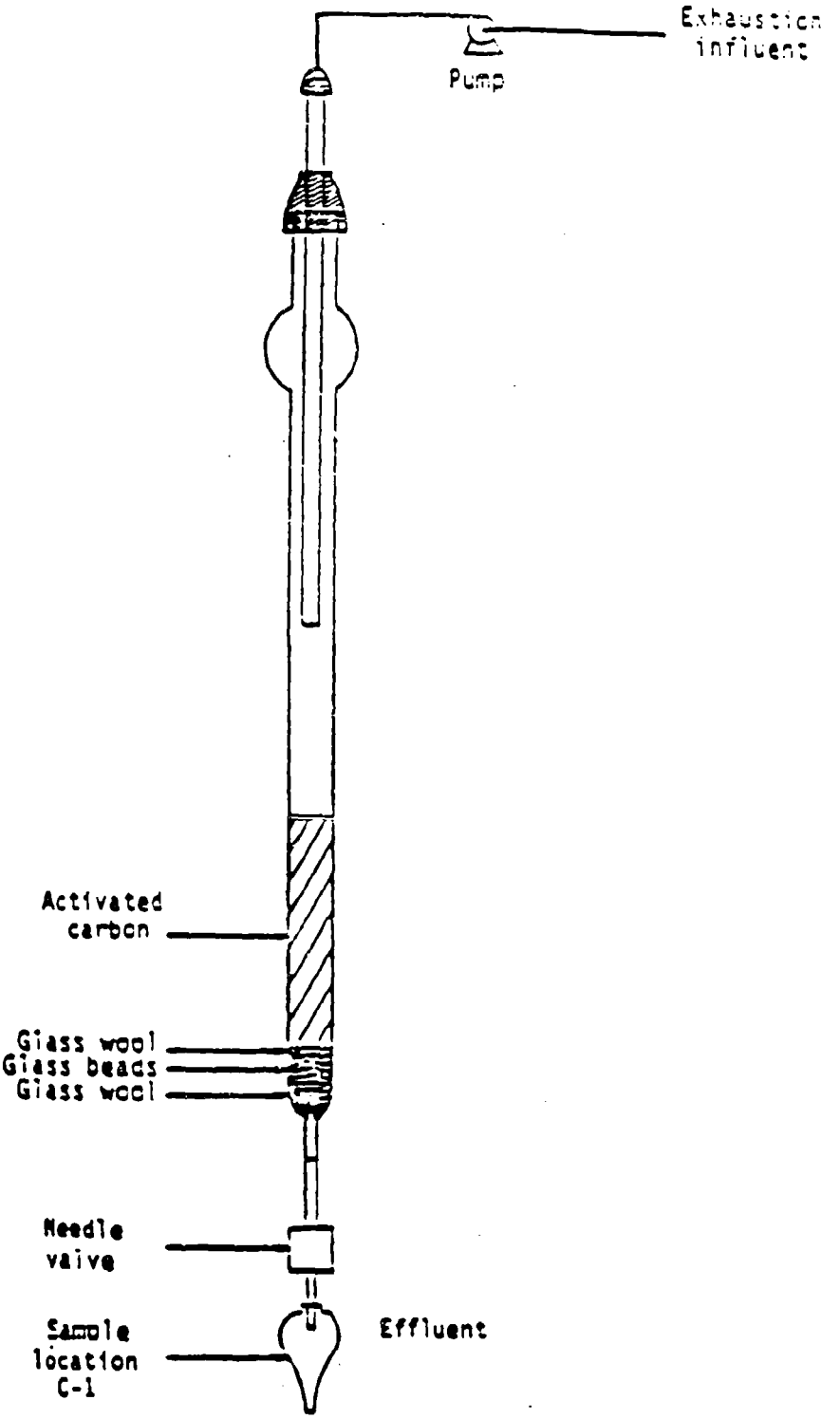


Figure 131. Flow diagram of granular activated carbon column

APPENDIX A
TEST PLAN - DNT TREATMENT TECHNOLOGIES

TEST PLAN - DNT TREATMENT TECHNOLOGIES

1. Introduction

This Test Plan has been prepared for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) in accordance with Contract Data Requirements List CDRL A005 under subcontract No. 897-88, PNB 3769-2-A. The objective of this project is to identify and develop the technology for removal of dinitrotoluene (DNT) from wastewaters by performing bench-scale testing of selected technologies [ultraviolet radiation (UV), ozone and granular activated carbon (GAC)]. This testing will provide economic data for comparison of the two treatment technologies. The work will be performed by PEI Associates, Inc., with assistance from Hercules Incorporated at Radford Army Ammunition Plant (RAAP), which will provide the bench-scale test facilities. The tests will be conducted during the period of April through June 1990.

1.1 Background

DNT, an ingredient used in the manufacture of single-base propellants, is a suspected carcinogen and has also been linked to heart disease by some studies. At present, a central biological wastewater treatment plant is operated at RAAP for treating wastewaters from propellant, nitroglycerin (NG), and other nitrate ester manufacturing processes. The NG and nitrate ester wastewaters are pretreated chemically prior to being combined with the propellant wastewater and treated biologically. Though the Virginia State Water Control Board has not established limits on DNT discharge, monitoring is required and DNT content in discharged wastewaters must be reported semi-monthly. Additionally, in the March 29, 1990 Federal Register, 2,4-DNT was listed as a constituent hazardous organic chemical. The level of regulatory concern for 2,4-DNT will be 0.13 mg/L and these requirements must be implemented by September 25, 1990. With recent changes in federal regulations and state requirements for monitoring DNT in effluents, it is clear that abatement facilities will become necessary.

A survey of the wastewater collection system was conducted which identified that water dry water represented the greatest source of DNT with solvent recovery, air dry, and coating operations providing additional though lesser amounts.

Analysis of the effluent stream from the biological treatment plant revealed the presence of occasional concentrations of DNT. Also no detectable quantities of DNT were found in the biomass.

DNT/biomass studies conducted under laboratory conditions determined that DNT did not exert a toxic or inhibiting effect on acclimated biomass from the biological treatment facility. Biomass studies were performed with two bioreactors; the first bioreactor was not exposed to DNT (blank) and the second exposed to DNT. Analysis by high performance liquid chromatography (HPLC) indicated no DNT, but the presence of several transformed by-products from DNT degradation. Toxicity studies were accomplished with wastewater respirometers measuring biological oxygen

demand (BOD) to assess repression of microbial respiration. Little or no toxicity was observed at concentrations of 100 mg/L.

A survey was conducted to identify technologies available for both destruction in wastewaters and DNT removal methods. The decomposition of DNT and its associate by-products from various treatment methodologies were reviewed whenever available in the literature. Approximately 50 articles were located and reviewed. Some articles contained little or no specific information related to DNT; however, they either provided insight into treatment technologies or information on treatment technologies for similar compounds.

Based on the literature reviewed, the following methods were recommended for evaluation: (1) various combinations of UV, ozone, and hydrogen peroxide treatment since they could provide an economical, easy to install operation, with low operator involvement; and (2) GAC and regeneration since laboratory work has demonstrated that GAC is able to remove DNT from wastewater, and a potential regeneration method could greatly improve its economics. Additionally, discussions with various vendors indicate that GAC was very effective in removing 2,6-DNT from wastewater.

Laboratory evaluations (performed at RAAP) of the technologies recommended from the literature review, indicated that bench evaluations of UV/ozone and biological (RBC) treatment held the greatest potential for successful and economical treatment of DNT containing wastewaters. No laboratory work was performed with GAC due to experience gained from previous projects involving TNT (and DNT as a contaminant).

1.2 Objective

The objective of this task is to continue the development of a technology for removal of DNT from wastewater through bench-scale UV/ozone and GAC tests of these wastes. Specifically, the following items will be addressed:

(1) Amount and characteristics of the DNT after treatment.
(2) Attempt destruction of the by-products detected qualitatively during HPLC analysis of DNT.
(3) Determine optimum operating conditions for bench equipment utilizing water dry wastewater.

RAAP will furnish the DNT wastewaters for these tests.

2. Technology Evaluations

2.1 Descriptions of Treatment Systems

UV/ozone

Oxidation is a chemical reaction that either increases the oxygen content or reduces the number of electrons of a compound. In wastewater

treatment, this leads to the destruction of waste compounds by the formation of new compounds. In a system where complete breakdown occurs, the by-products are carbon dioxide and water. UV, ozone, and hydrogen peroxide are various oxidation agents. UV provides a quantum of radiation that facilitates the breakdown of molecules by the excitation of electrons into less stable electron orbitals, while ozone and hydrogen peroxide chemically react with the molecules.

A Normag Photoreactor will be utilized for these bench studies (fig. 1). It has a height of 700-mm, width of 260-mm, and a depth of 100-mm. The 350-400 mL capacity reactor uses forced liquid circulation with a glass pump and Hostaflon-coated pump rotor. Liquid above the pump is sucked down, thrown outwards by the rotor at the bottom of the reactor, forced up through the riser pipe and fed back to the reaction vessel through the upper end of the pipe. The formation or consumption of gas can be monitored very precisely in the completely closed apparatus. The jacketed reaction vessel allows exterior heating or cooling.

Two types of UV radiation sources will be utilized with the Normag photoreactor. A mercury low-pressure lamp will produce intense radiation at the 254-nm mercury-resonance line. A mercury high-pressure lamp will be used to emit the characteristic mercury-line system which extends from the short-wave UV range of about 240-nm to well into the visible range. The strongest line is 366-nm.

The ozone will be made using oxygen flowing through an Airox Ozonator model C2P-3C-2 by Pollution Control Industries Inc.

Synthetic wastewater will be evaluated initially to separate and quantify the effects of several parameters which would be difficult to quantify in wastewater (table 2). Tests 1 through 12 will vary only the addition of ozone. This will assist in designing treatment facilities that maximize ozone addition since some locations may contain low quantities of organics to consume the ozone. Tests 13 through 15 will evaluate the effects of the high pressure lamp to compare its effectiveness in relation to the low pressure bulb. Tests 16 through 27 will evaluate the effects of solvents on UV utilization and ozone consumption. Tests 28 through 30 and additional testing will determine design requirements for treatment facilities and provice data for economic analysis based on actual wastewater.

Granular Activated Carbon

Filtrasorb 400 GAC from the Calgon Carbon Corporation will be utilized for the adsorption studies. A 1-inch diameter column (20-inch height) utilizing water dry wastewater will be used for the GAC column studies. The column is shown schematically in figure 2. The bed volume in the column will be designed to achieve a contact time of 30 minutes or greater. (Note: Isotherms will be performed on each batch of GAC for comparison purposes.)

The proposed operating conditions (flow rate, total volume, and direction of flow) for the GAC tests are presented in table 1. The GAC will be

backwashed with 2½ times the bed volume of distilled water before each test to remove all fine particulates, air pockets, and stratify the carbon bed. The proposed exhaustion flow rate for the GAC studies will be 3 mL/min. Exhaustion will be performed by downflow. An automated sample collector will be used to collect samples. Since the GAC will be exposed to varying quantities of solvents in the wastewater due to the processing of different propellant formulations, the exhausted column for tests 1 through 3 will be fed a solution containing 4.0 wt % solvents (2.0% ethyl alcohol and 2.0% ether) to determine if the solvents can displace the DNT from the GAC. For tests 4 through 6 the GAC will be exposed to the high solvent concentrations in wastewater to ascertain if their continuous feed will affect the adsorption of DNT.

2.2 Operational Data

UV/ozone

The variables with UV/ozone will consist of the use of two different UV bulbs, solvents (ethyl alcohol/ether), collection of samples at various time intervals, and periodic assessment of ozone addition. A low-pressure mercury lamp will produce 254-nm radiation. A high-pressure mercury lamp will produce from 240-nm to the visible range. Testing will be performed without solvents and with solvents (2.0 wt % ethyl alcohol and 2.0 wt % ether). Tests will be performed utilizing both bulbs, while samples are withdrawn at various time intervals. The flow rate and concentration of ozone will be monitored. Additionally, adsorption at 254 nm will be recorded for each wastewater (synthetic or actual) to quantify the differences in UV adsorption characteristics. Figure 3 represents a data collection form for UV/ozone testing.

Activated Carbon

Effluent DNT concentrations, flow rate, and time will be monitored for the GAC studies. Figure 4 represents a data collection form for the GAC column studies.

3. Sampling Plan

The primary objectives of these tests are to: (1) determine the effectiveness of each treatment technology in DNT pollution abatement; (2) determine the optimum operating parameters; and (3) determine the economics associated with each technology. RAAP will perform all tests and collect and analyze required samples and operational data as described herein; RAAP testing facilities will be used. This section describes the bench test program that will be implemented to meet these objectives.

3.1 Testing Program

UV/ozone

Synthetic wastewater (optical density at 254 nm will be recorded for comparison to actual water dry wastewater) will be prepared by mixing

100 mg/L DNT in distilled water. The Mormag photoreactor will be filled with either the synthetic or actual water dry wastewater (350 to 400 mL capacity). The selected UV bulb (two options) will be inserted and the ozone generator (three flow rates) precalibrated prior to operation. The glass pump with the Hostaflon-coated rotor will be started. Both the photoreactor and the ozone generator will be started at time 0. Samples will be collected at 0 (blank), 0.25, 0.5, 1.0, 5.0, 10.0, and 15.0 min (see table 2). Upon completion of testing on synthetic wastewater, testing will be performed on actual water dry wastewater utilizing optimum destructive conditions.

Activated Carbon

After backwashing the GAC in the column with distilled water, either actual water dry wastewater or synthetic wastewater prepared by mixing 100 mg/L DNT in distilled water will be utilized to saturate the GAC (tests 1 through 3). A reservoir will be filled with the wastewater and a pump will meter the flow to the column at 3.0 mL/min. The GAC will first be completely immersed in the wastewater. The needle valve of the column will then be adjusted to allow for the 3.0 mL/min elution flow rate of the evaluation. A sample collector will be operated to collect 10 mL samples until completion of the evaluation. Additional testing will be performed to determine if solvents in the wastewater streams remove DNT from GAC or affect adsorption capacity. To evaluate if the solvents can desorb DNT, the previously described steps utilizing water containing approximately 4.0% solvents by wt (estimated maximum that the carbon would be exposed to) will be followed. To evaluate the solvents effect on adsorption capacity, DNT and solvents will be processed (tests 4 through 6) at the same time utilizing the previously described steps.

3.2 Sampling

UV/ozone

Figure 5 contains a flow diagram of the UV/ozone reactor and the sample locations. Sample location UV-1 is where 10-mL samples will be taken at time intervals of 0 (blank), 0.25, 0.5, 1.0, 5.0, 10.0, and 15.0 minutes. Sample location UV-2 is where ozone flow rates will be collected.

Activated Carbon

Figure 2 contains a flow diagram of the GAC column and the sample location. Sample location C-1 is where 10-mL samples will be collected by a sample collector until DNT is detected above 0.5 mg/L. This will be accomplished by allowing the sample collector to fill 20 to 40 test tubes while processing the wastewater through the column. These test tubes will be labelled and delivered to the Technical Analytical laboratory where the two tubes sampled last will be analyzed. If no DNT is detected, no further analysis will be performed. If DNT is detected, tubes will be analyzed until at least two adjacent tubes contain no DNT.

4. Analytical Plan

4.1 Analytical Methods

The specific analysis that will be conducted on each sample has been defined upon review of the analytical results of previous work on this project and consultation with published literature. The analytical method that will be used for the detection of DNT and potential by-products (appendix 1) will utilize high performance liquid chromatography (HPLC). Wastewater samples will be diluted 50/50 with methanol to dissolve any particulate DNT and filtered to remove any additional suspended particulate matter and stored at room temperature for less than three hours. A series of ten standards encompassing the range from 0 to 200 mg/L DNT will be prepared for calibration of the HPLC. After calibration of the HPLC, samples from the evaluations (UV/ozone and activated carbon) will be processed and followed by a final check of the calibration with a known standard.

4.2 Quality Control/Quality Assurance (QC/QA)

A variety of quality control samples will be utilized throughout the laboratory testing and analysis process. These samples will utilize replicates, blanks, and/or spikes to monitor the quality of sample analysis. At least one blank will be performed on each test. Additionally, a replicate will be performed for each ten analyses and one spike will be performed for each ten analyses. Thus, the procedures used will not adhere to those specified in the "Sampling and Chemical Analysis Program" of the U.S. Army and Toxic Hazardous Materials Agency (December 1985) guidelines.

Mr. James Heffinger is RAAP's project engineer for this effort. Mr. Peter Hartmann is RAAP's Technical Analytical laboratory supervisor and is responsible for tracking analytical progress and ensuring timely completion of analysis. Both Messrs. Heffinger and Hartmann will review all sampling, analysis, and quality control prior to the start of this program. Subsequently, Mr. Heffinger and Mr. Hartmann will review the ongoing analysis of samples to ensure that cited methods are followed, that adequate quality control data are generated, and, if necessary, appropriate corrective actions are taken.

5. Data Analysis and Reporting

A detailed report summarizing the project background, objectives, experimental methods, results, and conclusions will be prepared at the conclusion of the test. This report will reference other project deliverables, such as the Program Plan and this Test Plan, and will document all aspects of the project. The operational and analytical data collected will be presented in appendices as unreduced data. A summary of the QC/QA protocols and results will be included. The data will be interpreted with regard to the following questions:

(1) How effective is the process in DNT removal?

(2) Are the by-products formed further degraded by additional treatment or do they accumulate?

(3) If possible from available data, which process is most cost effective?

Table 1. Operating conditions for activated carbon studies

Test no.	Activated carbon	DNT (mg/L)	Step	Flow rate (mL/min)	Total volume (bed volume)	Direction of flow	Elution solvent (% by wt)
1	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	?
		0	elution	3.0	?	down	2% ethyl alcohol 2% ether
2	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	?
		0	elution	3.0	?	down	2% ethyl alcohol 2% ether
3	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	?
		0	elution	3.0	?	down	2% ethyl alcohol 2% ether
4	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	2% ethyl alcohol 2% ether
5	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	2% ethyl alcohol 2% ether
6	FS-400	0	backwash	0.75	2-1/2	up	0
		100[1]	exhaustion	3.0	?	down	2% ethyl alcohol 2% ether

[1] 100 mg/L in wastewater.

Table 2. Test matrix for DNT degradation by UV/ozonation[1]

Test No.	Desired DNT conc (mg/L)	UV bulb type	Ozone flow rate (SCFM)	Solvents in water (wt %)
1	100	low	0	0
2	100	low	0	0
3	100	low	0	0
4	100	low	5	0
5	100	low	5	0
6	100	low	5	0
7	100	low	10	0
8	100	low	10	0
9	100	low	10	0
10	100	low	15	0
11	100	low	15	0
12	100	low	15	0
13[2]	100	high	10	0
14[2]	100	high	10	0
15[2]	100	high	10	0
16	100	optimum	0	2.0% ether, 2.0% ethyl alcohol
17	100	optimum	0	2.0% ether, 2.0% ethyl alcohol
18	100	optimum	0	2.0% ether, 2.0% ethyl alcohol
19	100	optimum	5	2.0% ether, 2.0% ethyl alcohol
20	100	optimum	5	2.0% ether, 2.0% ethyl alcohol
21	100	optimum	5	2.0% ether, 2.0% ethyl alcohol
22	100	optimum	10	2.0% ether, 2.0% ethyl alcohol
23	100	optimum	10	2.0% ether, 2.0% ethyl alcohol
24	100	optimum	10	2.0% ether, 2.0% ethyl alcohol
25	100	optimum	15	2.0% ether, 2.0% ethyl alcohol
26	100	optimum	15	2.0% ether, 2.0% ethyl alcohol
27	100	optimum	15	2.0% ether, 2.0% ethyl alcohol
28	wastewater	optimum		
29	wastewater	optimum		
30	wastewater	optimum		

[1] Additional testing will be performed as determined necessary for economic and design requirements.

[2] Testing with the high pressure bulb will be expanded if results are successful.

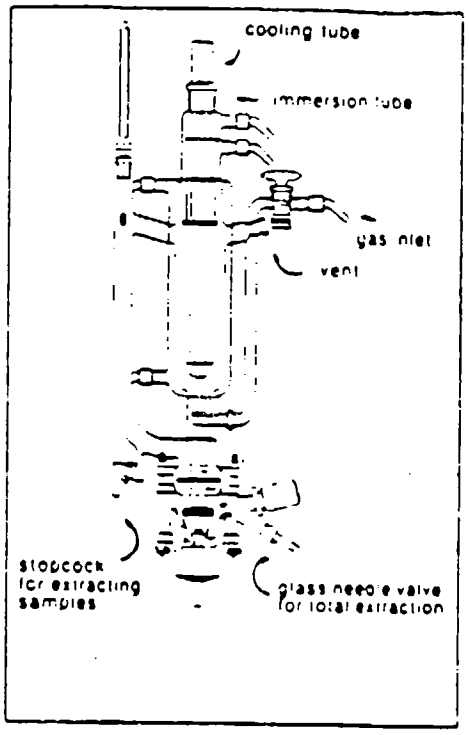


Figure 1. Normag photoreactor

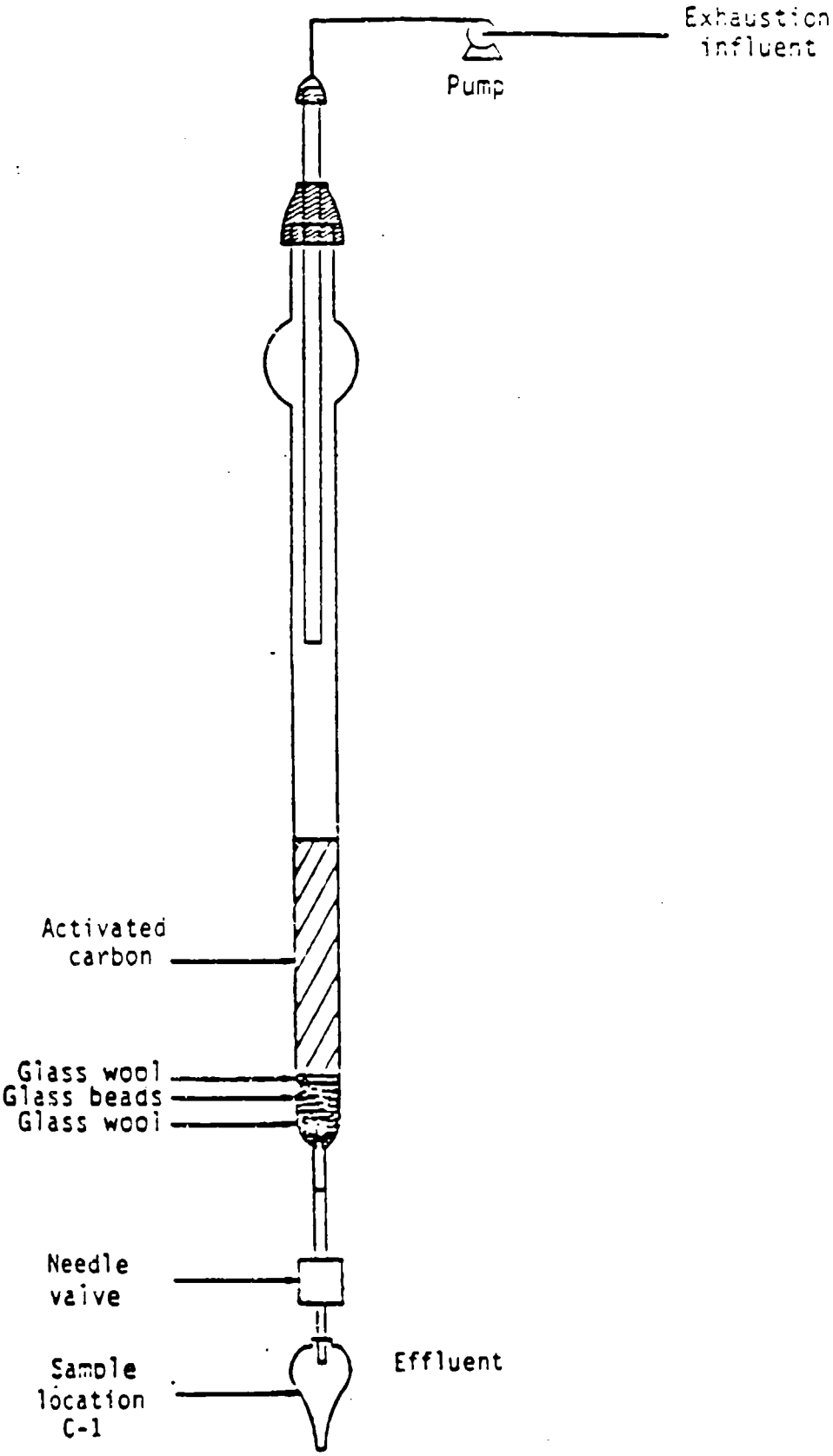


Figure 2. Schematic of column

Figure 3. Data collection form for UV/ozone testing

			Sample time (min)						
Test No.	OD 254	Bulb	1/4	1/2	1	5	10	15	Ozone flow rate

Figure 4. Data collection form for GAC studies

Test No.	OD 254	Sample No.	Column feed (DNT or solvent)	DNT concentration (mg/L)	Flow rate (mL/min)

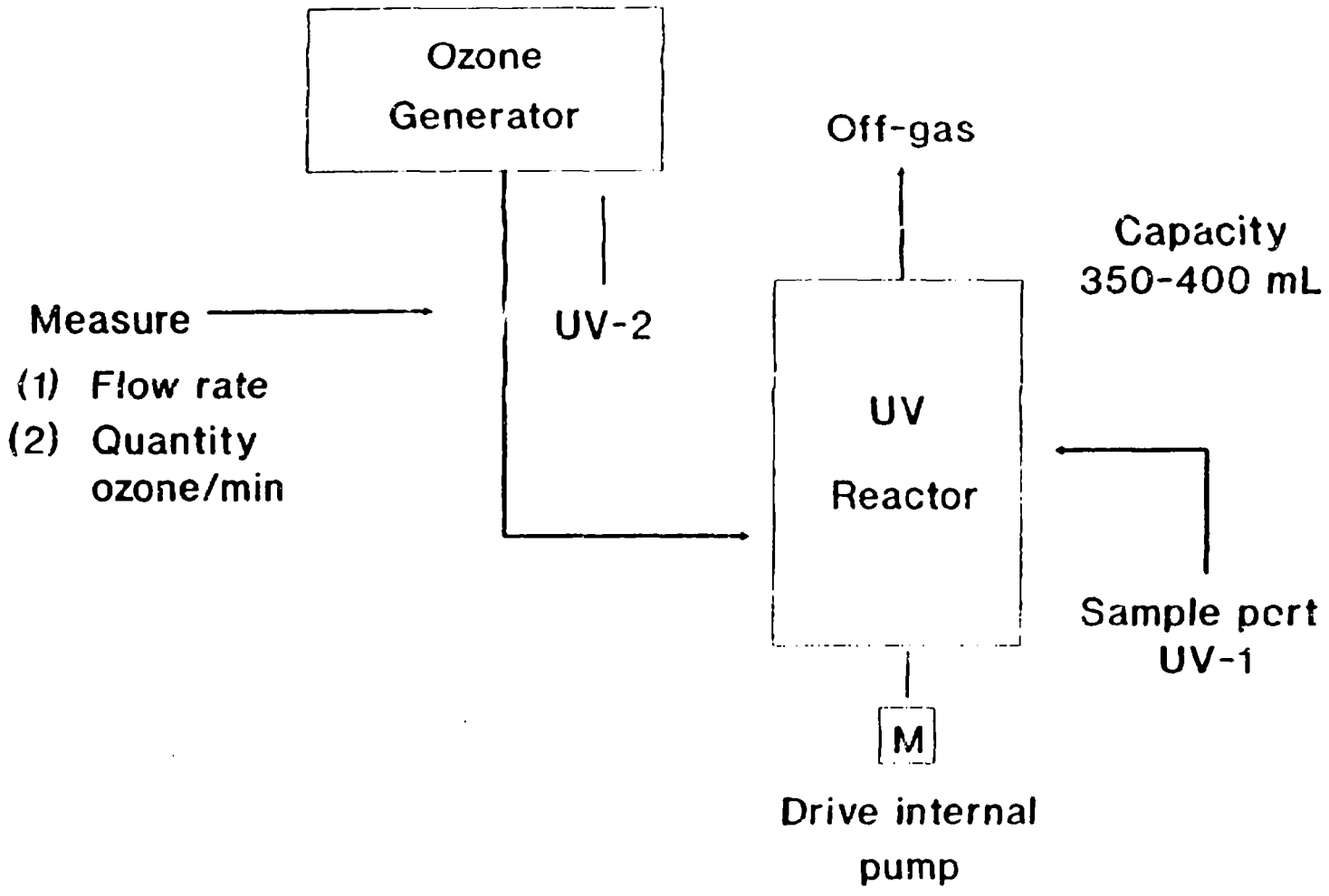


Figure 5. Batch UV/ozone studies

HERCULES

RADFORD ARMY AMMUNITION PLANT

Safety is part of your job.

Memorandum

March 23, 1990

ATTACHMENT 1

cc: C. D. Chandler
L. R. Gizzi
L. L. Smith
P. J. Hartmann
File

TO: J. G. Heffinger

Test Plan for PEI Associates, Inc.

Attached is the proposed test plan for analysis of dinitrotoluene (DNT) in wastewater, to be submitted to PEI Associates, Inc. Since EPA Method 625 is a gas chromatography/mass spectrometry method and NIOSH Method S215 is for the analysis of DNT in air samples, a liquid chromatographic method is proposed for use in this study.

If a sample of DNT could be obtained from the USATHAMA Standard Analytical Reference Materials (SARM), it would prove beneficial for traceability purposes.

LHM/as

Attachment

Sample Preparation

Prior to analysis, wastewater samples will be filtered through a 0.45 m filter to remove suspended particulate matter. Samples will be stored at ambient temperature until analyzed. Analysis will occur within three hours.

Standard Preparation

A series of ten standards encompassing the range from 0 to 200 parts per million DNT will be prepared and chromatographed by the method below.

Chromatographic Method

The samples and standards will be analyzed by an isocratic HPLC method. The chromatographic conditions are listed below:

Instrument:	Hewlett Packard HP 1090 Liquid Chromatograph
Column:	25 cm Lichrosorb RP-18 4.6 mm i.d.
Mobile Phase:	55% Methanol/45% Water
Flow Rate:	2.00 mL/min
Oven Temperature:	40°C
Reservoir Temperature:	ambient
Injection Volume:	normally 250 µL
Detector:	Hewlett Packard 1040A Diode Array Detector at 254 nm/550 nm reference

Statistical Analysis of the Analysis Method

Three injections of each standard will be made, and a plot of area vs. concentration made. Linear regression analysis should reveal the correlation coefficient to be at least 0.990.

The highest, lowest, and mid-range standards will be subjected to a test for precision of the analysis method. Each of these standards will be injected and chromatographed ten times. The area count, for each standard, as determined by the integrator, will be averaged and the mean, standard deviation and relative standard deviation will be determined. Relative standard deviation will be less than 5% in the most used (low to mid-range) portion of the calibration curve.

Statistical Analysis of the Analysis Method (contd)

The accuracy of the method will be determined by chromatographing known (weighed) amounts of DNT and comparing the calculated amount (from the calibration curve) to the known amount in the following manner:

$$\% \text{ inaccuracy} = \frac{\text{known} - \text{calculated}}{\text{known}} \times 100$$

Percent inaccuracy will be less than 7 percent in the most used portion of the calibration curve.

The minimum detectable quantity (MDQ), or detection limit will also be determined by injecting lower and lower amounts of DNT onto the chromatographic column. The lowest amount of DNT recognized as a peak by the integrator, at its most sensitive setting, will be considered the MDQ. Additionally, visual inspection of the chromatogram must reveal the peak to be at least three times the noise level of the baseline. The MDQ should be at least 0.2 µg.

APPENDIX B
STATISTICAL ANALYSIS OF THE ANALYSIS METHOD

HERCULES

RADFORD ARMY AMMUNITION PLANT

Safety is part of your job.

Memorandum

July 17, 1990

c: C. D. Chandler
L. R. Gizzi
P. J. Hartmann
File

TO: J. G. Heffinger, Engineer
Process Engineering

Per test plant dated March 23, 1990 to J. G. Heffinger from L. H. McDaniel entitled (Test Plan for PEI Associates Inc.), 10 standards of 2,4-DNT (HPC Lot 1560) were weighed individually ranging from 0.0000 grams blank to 0.0200 g and placed in 50 mL HPLC grade methanol with 50 mL deionized H_2O. Each standard was then filtered thru a Millex-5R 0.5 μm filter before being analyzed according to following chromatographic conditions:

Instrument: Hewlett Packard HP-1084B Liquid Chromatograph

Column: 25 cm Lichrosorb RP-18 4.6 mm i.d.

Mobile Phase: 55% Methanol/45% Water

Flow Rate: 2.00 mL/min

Oven Temperature: 40°C

Reservoir Temperature: Water 80°C Methanol 40°

Injection Volume: 20 μL

Detector: 254 nm/430 reference

WCJ/as

Attachments

Statistical Analysis of the Analysis Method

Three injections of each standard were performed, plotting the area versus the concentration. The linear regression analysis showed the correlation coefficient to be 0.9974. Table I gives the results for all ten samples. Four of the standards (0.0010 g/100 mL, 0.0052 g/100 mL, 0.0078 g/100 mL, 0.0107 g/100 mL) were subjected to a test for precision of the analysis method. Each was injected and chromatographed 10 times. Table II gives the results obtained. As can be seen in Table II, the highest relative standard deviation obtained was 2.6%.

The accuracy of the method was determined by chromatographing four known (weighed) amounts of DNT and comparing the calculated amount (from the calibration curve) to the known amount weighed. The percent inaccuracy ranged from 0.06% to 5.5%, well below the 7.0% listed in the memo. Table III shows the results of the accuracy test.

The minimum detectable quantity (MDQ) was determined by injecting diluted samples of the lowest standard into the chromatographic column. The lowest amount detected under these test conditions was 1.2 mg per liter. Using 200 μL injections instead of 20 μL injections as in test conditions, 0.12 mg/L was the minimum amount detected.

TABLE I

Triplicate Analysis of DNT Standards on 1084B Liquid Chromatograph

Std. Wt. DNT g	Triplicate Results Area Count 1	2	3	Mean	RSD %
0.0000	0	0	0		
0.0005	22600	21710	22310	22206.6	2.04
0.0010	33650	37280	34210	35046.6	5.58
0.0025	93860	91820	91820	92500	1.27
0.0044	153300	150100	154500	152633	1.49
0.0052	197100	194600	195100	195600	0.68
0.0078	298800	305300	305400	303166	1.25
0.0107	413000	416900	412100	414000	0.62
0.0146	622700	619000	618900	620200	0.35
0.0200	769000	769200	773200	77046	0.31

Correlation Coefficient = 0.9974

TABLE II

Precision of DNT/LC Analysis Method

	10ppm Standard Area Count	52ppm Standard Area Count	78ppm Standard Area Count	107ppm Standard Area Count
	33650	195500	301000	433600
	34240	194000	302300	432200
	34210	189100	298000	429100
	33750	192200	298500	434200
	32940	189300	300000	433400
	34170	191600	303300	430000
	34360	193600	298700	425800
	32540	193200	299600	438800
	34960	191800	298400	433700
	35500	193800	301000	428300
Mean	= 34032	192410	300080	431910
Std. Deviation	= 873.16	2048	1788	3696
% RSD	= 2.6%	1.1	0.60	0.85

TABLE III

Accuracy of Method

From Cal. Curve ppm	Weighed Amount *ppm	Inaccuracy %
8.3727	8.00	4.7
52.7404	50.00	5.5
98.3585	100.00	1.6
102.360	103.00	0.6

* Standards were weighed in g/100ml and converted to ppm.

$$\% \text{ Inaccuracy} = \frac{\text{Weighed Sample - Amount from LC calib.} \times 100}{\text{Weighed sample}}$$

APPENDIX C
UV/OZONE TEST PLAN DATA

Tests 1-3

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	101.6	83.58	90.01	94.77
	94.32	90.91	89.86	92.77
	92.52	95.12	90.41	92.67
Std. deviation	3.93	4.77	0.23	0.97
Variance	15.41	22.74	0.05	0.94
Maximum	101.60	95.12	90.41	94.77
Minimum	92.52	83.58	89.86	92.67
Average	96.15	89.87	90.09	93.40

Tests 4-6

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	99.39	92.41	88.65	84.99
	94.72	88.25	88.95	85.09
	92.01	92.72	88.8	83.78
Std. deviation	3.05	2.04	0.12	0.60
Variance	9.29	4.15	0.01	0.35
Maximum	99.39	92.72	88.95	85.09
Minimum	92.01	88.25	88.65	83.78
Average	95.37	91.13	88.80	84.62

Tests 7-9

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	99.34	91.36	85.79	84.94
	93.42	94.37	89.1	84.99
	97.18	92.87	89.71	81.48
Std. deviation	2.45	1.23	1.72	1.64
Variance	5.98	1.51	2.97	2.70
Maximum	99.34	94.37	89.71	84.99
Minimum	93.42	91.36	85.79	81.48
Average	96.65	92.87	88.20	83.80

Tes. ,2

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	82.58	90.86	88.95	81.53
	96.68	91.61	90.56	83.93
	91.76	98.54	88.3	80.02
Std. deviation	5.84	3.46	0.95	1.61
Variance	34.14	11.95	0.90	2.59
Maximum	96.68	98.54	90.56	83.93
Minimum	82.58	90.86	88.30	80.02
Average	90.34	93.67	89.27	81.83

Tests 13-15

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	95.58	93.47	91.26	87.3
	98.49	90.66	90.26	91.86
	97.53	92.26	91.41	91.26
Std. deviation	1.21	1.15	0.51	2.02
Variance	1.47	1.32	0.26	4.09
Maximum	98.49	93.47	91.41	91.86
Minimum	95.58	90.66	90.26	87.30
Average	97.20	92.13	90.98	90.14

Tests 19-21

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	85.69	93.37	87.2	89.55
	106.97	91.56	86.05	84.29
	119.35	85.29	80.57	76.91
Std. deviation	13.90	3.46	3.34	5.18
Variance	193.23	11.99	11.18	26.88
Maximum	119.35	93.37	88.05	89.55
Minimum	85.69	85.29	80.57	76.91
Average	104.00	90.07	85.27	83.58

Tests 22-24

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	88.65	90.86	96.13	87.45
	86.85	144.9	91.51	79.92
	85.75	93.27	85.69	81.02
Std. deviation	1.20	24.93	4.27	3.32
Variance	1.43	621.31	18.25	11.03
Maximum	88.65	144.90	96.13	87.45
Minimum	85.75	90.86	85.69	79.92
Average	87.08	109.68	91.11	82.80

Tests 25-27

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	98.44	91.61	92.26	89.05
	96.78	95.78	91.16	89.4
	86.64	76.6	80.82	78.26
Std. deviation	5.22	8.24	5.15	5.17
Variance	27.20	67.84	26.56	26.74
Maximum	98.44	95.78	92.26	89.40
Minimum	86.64	76.60	80.82	78.26
Average	93.95	88.00	88.08	85.57

Irradiation of 25 mg DNT/L solution

	Time (min)			
	0	1	5	10
DNT conc. (mg/L)	23.82	22.52	21.06	17.06

Preliminary wastewater irradiation

	Time (min)					
	0	5	30	60	90	120
DNT conc. (mg/L)	191.01	172.15	134.96	103.2	84.79	65.82

Effect of varying ozone flow rate on destruction of DNT in wastewater

	Time (min)			
	0	5	35	65
DNT conc. (mg/L) at various ozone flows				
5 SCFH Ozone	105	90.51	62.96	46.92
10 SCFH Ozone	97.48	98.29	66.77	45.43
15 SCFH Ozone	108.12	91.76	62.01	44.34

Final ozone parameters for wastewater (Tests 28-29)

	Time (min)					
	0	5	65	125	185	245
DNT conc (mg/L)	143	87.6	47.84	26.21	10.18	0
	229.45	187.15	95.27	39.45	3.95	0
Std. deviation	42.88	49.78	23.71	6.62	3.11	0.0
Variance	1838.27	2477.55	562.40	43.82	9.70	0.0
Maximum	229.45	187.15	95.27	39.45	10.18	0.0
Minimum	143.70	87.60	47.84	26.21	3.95	0.0
Average	186.58	137.38	71.56	32.83	7.07	0.0

APPENDIX D
PRELIMINARY HAZARDS ASSESSMENT

HERCULES
RADFORD ARMY AMMUNITION PLANT

Safety is part of your job.

Memorandum

June 28, 1990

HI-90-M-068
Preliminary Hazards Assessment of
Technologies to Remove DNT from RAAP Wastewaters

Objective

The objective of this study is to hazards assess technologies to remove dinitrotoluene (DNT) from process wastewater being developed under Process Engineering (PE) project 277, Removal of DNT from RAAP Wastewaters. This report identifies and evaluates potential hazards to personnel and facilities during laboratory testing.

Summary and Conclusions

A preliminary hazards analysis (PHA), shown in Table 1, was conducted on two technologies being developed to remove trace amounts of DNT from process wastewater. Technologies assessed were: (1) an activated carbon absorption process, and (2) a bench scale ultraviolet (UV)/ozone photoreactor. It was determined that these systems are acceptably safe because they involve only limited sample volume, and quantities of DNT dissolved in water which are nonreactive concentrations. These laboratory tests involve ozone and ultraviolet radiation, which are not typical operations.

Safety precautions used include: shielding, UV goggles, and ozone bubbled through water to decrease concentration. Personnel exposure to these agents must be monitored and controlled.

ADDENDUM I

Recommendations

Recommendations to enhance the safety of DNT removal operations are presented in Table 2.

Future Work

No future work is planned under this subcontract.

INTRODUCTION

DNT is used in the manufacture of single-base propellants. DNT has been listed as a hazardous organic chemical, and wastewater discharged after September 1990 must have a DNT concentration of 0.13 mg/l or less. Thus, abatement facilities are necessary.

Now process wastewater is treated at the biological wastewater treatment plant. This plant does not effectively remove DNT. Therefore new technology must be developed to remove DNT. Two technologies are being investigated by Process Engineering: (1) an absorption process using activated carbon, and (2) a UV/ozone photoreactor to chemically degrade DNT.

A PHA was performed on laboratory scale DNT removal equipment and proposed operations to provide safety design criteria in the event of scale-up. The results are shown in Table 1, and the recommendations are extracted and listed in Table 2 for clarity.

DISCUSSION

Material Response

The DNT removal studies will be conducted using sample sizes of approximately one liter of water containing up to 350 mg of DNT. As seen in Table 3, 350mg/l is insoluble in water. The Process Engineering study test data indicates a slightly higher solubility. The purpose of the excess DNT is to maintain a saturated solution at all times and this is done by constant agitation of the feed solution.

Material response data is presented for DNT in Table 4. The data for DNT is presented to illustrate that dry DNT is somewhat reactive, but when 350 mg are dissolved in a liter of water, it is nonreactive. As seen, DNT is fairly insensitive to mechanical, thermal, and shock stimuli, while DNT in solution is insensitive to all stimuli listed.

Table 5 presents thermal test data for activated carbon containing TNT and DNT. These tests consisted of 68.8% activated carbon and 31.2% organic contaminants. This data indicates that spent activated carbon is insensitive to thermal stimuli, and does not present a detonation hazard under these conditions. The solution used in the DNT removal studies will not contain TNT, nor will the DNT concentration be as high. Thus, the test activated carbon is expected to be less sensitive than the activated carbon data shown in Table 5.

Absorption Process

Insufficient DNT is present for an explosive reaction. The granular activated carbon (GAC) column, depicted in Figure 1, has several safety features to minimize risk to personnel and facilities (see Appendix A for a process description). The safety features include: (1) low concentration of DNT dissolved in water, and (2) limited sample size.

Personnel hazards were identified as a result of this study. As seen in Table 1, personnel will be exposed to alcohol and DNT. However, wearing of needed protective equipment will eliminate this concern.

The compatability of DNT with the activated carbon will also have to be determined. Previous tests determined that TNT is incompatible with activated carbon. However, as seen in Table 5, TNT did not react with the activated carbon even at high temperatures. To prevent reaction, the activated carbon will be wet and the tests will be performed at ambient temperatures.

UV/Ozone Photoreactor

The UV/ozone photoreactor, depicted in Figure 2, will break down the DNT into new compounds. If complete break down occurs, the by-products are carbon dioxide and water. UV provides a quantum of radiation that excites electrons into less stable orbitals, which in turn facilitates the break down of molecules. The ozone will chemically react to oxidize the molecules. For a complete process description see Appendix B.

Insufficient DNT is present for an explosive reaction. However, as seen in Table 1, three concerns were identified as a result of this study: (1) exposure to UV radiation/light, (2) ozone levels within the lab, and (3) thermal hazards as a result of the reaction. Safety features designed to minimize these hazards are: the reactor will be shielded to prevent personnel exposure from UV radiation/light. However, the UV radiation will have to be monitored to comply with the Army requirement of 1 mw/cm^2 for periods greater than 16 minutes.[1]

The ozone will be used under an enclosed hood to prevent the gas from escaping. Currently, personnel do not have the capability to measure ozone levels. An instrument must be purchased to monitor the ozone levels within the lab, which must be lower than 0.20 mg/m^3 or 0.1 ppm^2.

As seen in Table 1, thermal hazards are not a concern because the reactor will be jacketed in order to precisely control the temperature. In the event that the thermometer fails or is broken, it can be easily replaced since it is external to the reaction.

A problem common to both test procedures is disposal of the DNT solution. Since the waste treatment facility is not equipped to handle DNT, it is suggested that the solution be kept in a waste container and disposed of accordingly.

REFERENCES

[1]AR 40-46, "Control of Health Hazards from Lasers and Other High Intensity Optical Sources," Headquarters, Department of the Army, Washington, D.C., 6 February 1974.

[2]Threshold Limit Values and Biological Exposure Indices for 1989-1990, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.

Table 1

Preliminary Hazards Analysis of Technologies to Remove DNT from BAAP Wastewater

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Advantages	Suggestion Action
Building 4702	a. Building not rated for explosives	The maximum concentration of DNT will be 125 mg per liter of water, which is nonreactive	None	Operations does not have explosive building requirements	
	b. Ozone generated in building	Ozone generated will be used under an enclosed fume hood	None	Will remove fumes	
		Ozone will be bubbled through water	None	Reduces ozone concentration	
	c. Drains plugged	DNT is not to be put into drains	None	Treatment plant cannot handle DNT	
Granular Activated Carbon Absorption System	a. Exposure to alcohols	Goggles are required	None	Prevents alcohol from getting into eyes	
	b. Compatability of granular activated carbon with DNT		Compatability test required	Assure that GAC will not react with DNT	
	c. Exposure to DNT	Gloves required	None	Prevents skin contact with DNT	
	d. Control failure	Pump flow rate range is 0.36 ml/m to 36 ml/m	None	Limited sample size will prevent column from flooding immediately	
	e. Power failure	Solution in column would not be affected	None	Feed pump would shutoff - however, solution in column would not be affected	
	f. Broken column	DNT concentration is so low 125 mg/L water, that it can be safely cleaned up by operator wearing gloves and goggles	Column should be contained	This will prevent DNT from entering drainage system which empties into the sewage treatment plant, which is not equipped to handle DNT	

Table 1 (cont)

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Advantages	Suggestion Action
UV/Ozone Photoreactor	a. UV radiation	The photoreactor is shielded	None	Shielding prevents UV radiation from escaping photoreactor	Will be monitored to assure personnel exposure is below the Army requirement 1 mW/cm^2 for periods greater than 16 min[5]
	b. UV light	Photoreactor is shielded; UV goggles required	None	Shielding will prevent exposure to UV light	
	c. Ozone	Bubbled through water		Prevents escape into bay	An instrument must be purchased to measure ozone levels to assure they are below 0.1 ppm or 0.20 mg/m^3
	d Thermal Hazard	The photoreactor is jacketed to precisely control the temperature	None	Prevents overheating	
	e. Broken bulb	Bulb is contained within its own separate tube in the apparatus		Glass shards, etc contained	
	f. Nonfunctioning bulb	No UV reaction will take place	None	This situation will be detected when samples are analyzed for BHT concentration	
	g. Broken thermometer	The thermometer is external to the reaction	None	Can be easily replaced	

Table 2

Recommendations to Enhance Safety of ONT Removal Operations

Recommendation	Safety Benefit	M or S	Authority	Assigned to	Status
A. Equipment					
1. An instrument to measure ozone levels must be purchased	Ensure personnel exposure to ozone is below threshold exposure limit	M	Standard Safety Practice	Safety	Open
2. Contain granular activated carbon column so spill will not enter drainage system	Prevent ONT from reaching drain	M	Standard Safety Practice	PE	Open
B. Miscellaneous					
1. Determine compatability of granular activated carbon	Prevent reaction of ONT with GAC	M	Standard Safety Practice	PE	Open
2. Monitor the UV radiation emitted from photoreactor to assure it is below 1mW/cm^2	Ensure personnel exposure to UV radiation is below the threshold exposure limit	M	Standard Safety Practice	Safety	Open
3. Monitor the ozone level in the lab to assure it is below 0.1ppm or 0.20 mg/m^3	Ensure personnel exposure to ozone is below the threshold exposure limit	M	Standard Safety Practice	Safety	Open

Table 2 (cont)

Recommendation	Safety Benefit	M or S	Authority	Assigned to	Status
B. Miscellaneous (cont)					
4. Keep waste DNT in a waste container to be disposed of accordingly	Prevent DNT from reaching waste treatment facility	S	Standard Safety Practice	PE	Open

Adoption - Verification Schedule

A. Adoption Schedule

	Date
1. All items	9/90

B. Verification Schedule

One work week after notification is received from assigned department.

Table 3

Solubility of DNT in Water[a] at Different Temperatures

Temperature (°C)	% Solubility	g/L
22	0.027	0.0027
50	0.037	0.0037
100	0.254	0.0254

[a]Data from Engineering Design Handbook, Explosive Series Properties of Explosives of Military Interest, Headquarters US Army Material Command, January 1971.

Table 4

Material Response Data for DNI[a]

Formulation	Physical Condition	Threshold Initiation Level[b] Impact ft lb/in²	Friction psi @ 8 fps	ESD J	Critical Height	Critical Diameter	Shock	Onset Temp°C
DNI	Flake	60	>83,500	1.26	>48 in @ 2 in diameter	<0.25 in	NR[c]	307
DNI	125 mg/l water	NR	NR	NR	NR	NR	NR	NR

[a]Data from Hazards Analysis Memorandum MI-88-M 005, January 15, 1988.

[b]The TIL is defined as the highest energy level which produced no initiations in 20 consecutive trials, with at least one initiation occurring at the next higher test level

[c]No reaction with No. 8 blasting cap.

Table 5

Thermal Test Data for Activated Carbon, TNT, and DNT[a]

Confinement	Material Quantity[c]	Heating Time[d]	Temperature[e]	Description of Reaction
Confined (both[b] ends capped)	8.4 lb	17 min	Center of material: 215°F Inside pipe wall: 295°F Outside pipe wall: 480°F	Hissing noise. Reaction gases vented through thermocouple ports, spewing a small quantity of material out of the test pipe.
Unconfined[b] (top of pipe open to atmosphere)	7.3 lb	23 min (smoke) 25 min (flame)	Center of material: 260°F Inside pipe wall: 410°F	Smoke for approximately 2 min accompanied by spewing of material out the top of the pipe for the last 15 s. Followed by flame up to 8 ft out the top of the pipe lasting for 15 s. Smoke then continued for several more minutes.[f]

[a]Data extracted from Hazards Analysis Memorandum, HI-89-M-040, May 9, 1989.

[b]Tests were performed in a 4-in. diameter, 2-ft length of Schedule 40 seamless steel pipe. See Figure 3 for test setup.

[c]Material composition was 68.8% activated carbon, 15.6% TNT, 15.6% DNT, with approximately 0.5% moisture (water).

[d]Time from starting to heat the outside of the pipe until first indication of reaction.

[e]Temperature recorded immediately prior to first indication of reaction.

[f]Video coverage of this test is on file in the Hazards Analysis Department.

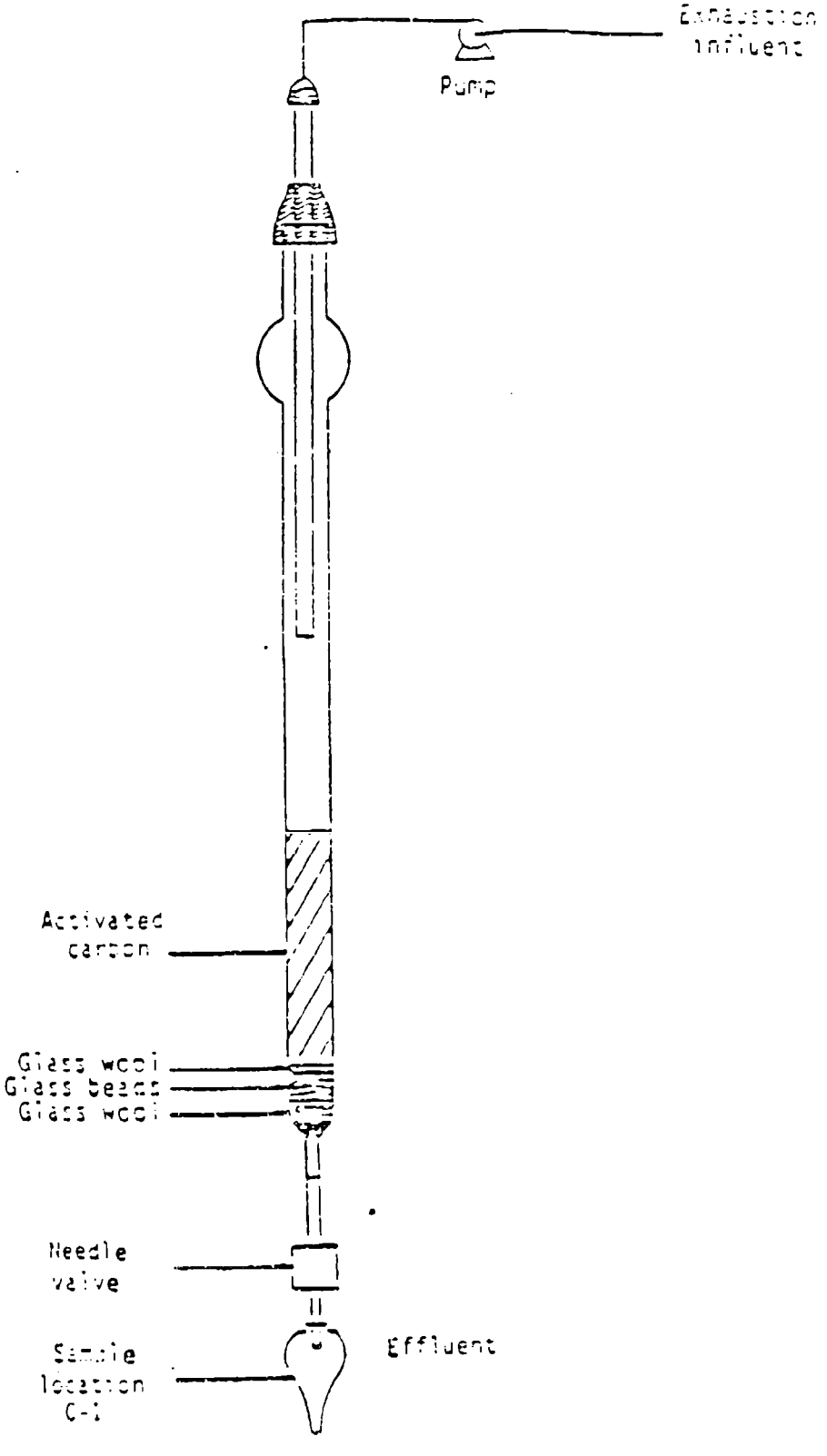


Figure 1. Schematic [illegible]

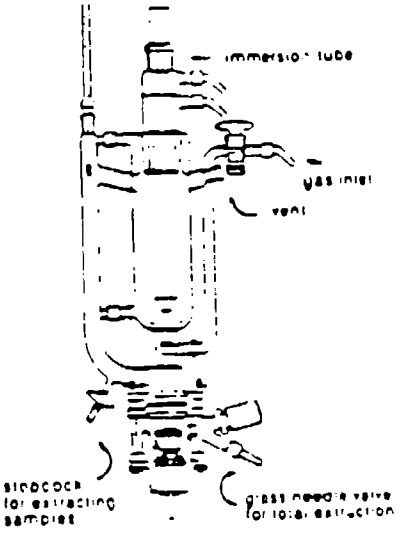


Figure 2. Norrag Photoreactor

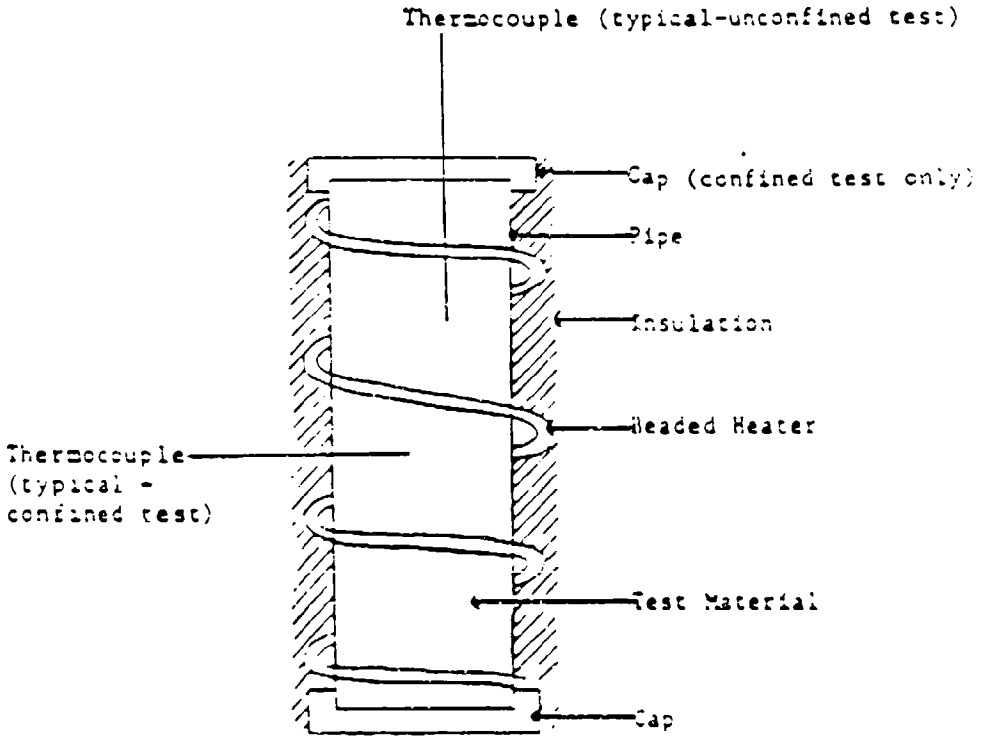


Figure 3. Test Setup for Thermal Tests

APPENDIX A

Granular Activated Carbon Absorption Process Description

The process for removing DNT from wastewater is described below. A one inch diameter column, depicted in Figure 1, will be packed with Filtrasorb 400 granular activated carbon from Calgon Carbon Corporation. The column will be packed so the DNT will contact the activated carbon for 30 minutes. The flow rate will be up to 3 mL/min. The column will be backflushed with 2 1/2 times the bed volume distilled water before each test to remove all fine particulates, air pockets, and to stratify the carbon bed. The proposed exhaustion flow rate, which will be performed by downflow, will be 3 mL/min. These tests will determine how many pounds of DNT will be absorbed per pound of granular activated carbon.

UV/Photoreactor Process Description

A Normag photoreactor, depicted in Figure 2, will be used in these studies. It has a height of 700 mm, width of 260 mm, and a depth of 100 mm. The reaction vessel will be jacketed to allow exterior heating or cooling. Ozone will be introduced through the gas inlet. The ONT/ozone solution will be circulated down past the radiation source, up the exterior tube, and back down past the radiation source.

The tests will consist of two types of UV radiation sources: (1) a mercury low pressure lamp, which produces intense radiation at 254 nm mercury resonance line, and (2) a mercury high pressure lamp used to emit characteristic mercury line system from about 240 nm to well into the visible range, with the strongest line being 366 nm.

The ozone will be produced using oxygen flowing through an Airox Ozonator Model C2P-3C-2 by Pollution Control Industries, Inc.