INEL-96/0151

April 1996

Idaho
National
Engineering
Laboratory

Decomposition of PCBs in Oils Using Gamma Radiolysis

A Treatability Study, Final Report

B. J. Mincher and R. E. Arbon

Lockheed
Idaho Technologies Company

INEL--96/0151

DECOMPOSITION OF PCBs IN OILS USING GAMMA RADIOLYSIS
A Treatability Study, Final Report

B.J. Mincher and R.E. Arbon

Published April 1996

Idaho National Engineering Laboratory
Lockheed Idaho Technologies Company
P.O. Box 1625, Idaho Falls, Idaho 83415-7111

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223

ABSTRACT

This report presents the results of a treatability study of radiologically and PCB contaminated waste hydraulic oils at the Idaho National Engineering Laboratory (INEL). The goal of the study was to demonstrate that PCBs could be selectively removed from the contaminated oils. The PCBs were selectively decomposed in an in-situ fashion via gamma-ray radiolysis. The gamma-ray source was spent nuclear fuel at the Advanced Test Reactor (ATR) canal at the Test Reactor Area (TRA), of the INEL. Exposure to gamma-rays does not induce radioactivity in the exposed solutions. The treatability study was the culmination of five years of research concerning PCB radiolysis conducted at INEL which investigated the mechanism and kinetics of the reaction in several solvents. The major findings of this research are summarized here. Based upon these findings three INEL wastestreams were selected for testing of the process. The Environmental Protection Agency (EPA) treatment standard of 2 $mgkg^{-1}$ was successfully achieved in all wastestreams. The interference of contaminants other than PCBs is discussed.

CONTENTS

FIGURES

TABLES

DECOMPOSITION OF PCBs IN OIL USING GAMMA RADIOLYSIS

INTRODUCTION

The radiation chemistry of the polychlorinated biphenyls (PCBs) and other halogenated hydrocarbons has received considerable study in a number of solvents. Among them have been water[1], alkaline isopropanol[2,3,4,5,6], neutral isopropanol[7,8,9] , cyclohexane[10], petroleum ether[11] and electrical insulating oils[12]. Interest in PCB radiolysis results from the need to understand the nature of PCB reaction products in irradiated foods[10,11] and the desire to design safer and more efficient disposal techniques[6]. This work will focus on the use of radiolysis as a potential waste treatment process. Current United States EPA approved treatment technology for PCBs requires the use of incineration or high efficiency boilers[13] however radiolysis has inherent benefits. Among the important benefits are the possibility of in-situ treatment, selective destruction of the PCBs and non-oxidizing treatment which prevents formation of undesirable products such as dioxins.

The most thoroughly studied solvent has been alkaline isopropanol. It is well known that in alkaline isopropanol decomposition proceeds rapidly via reductive, chain-reaction dechlorination to produce lesser chlorinated, "daughter" PCBs[5,6]. Upon continued irradiation non-chlorinated biphenyl is produced. Reaction rates (G values) in excess of 1000 molecules 100 eV^{-1} g^{-1} have been reported[6]. The radiation chemistry of isopropanol has been well studied and it is known that degradation of PCBs in alkaline isopropanol solution occurs as a result of attack by reactive reducing species generated by solvent radiolytic decomposition[6]. Dechlorination of PCBs in alkaline isopropanol is the result of electron transfer from the acetone radical anion which is generated from the α-hydroxy isopropyl radical by direct isopropanol radiolysis under only alkaline conditions[6]. The series of reactions is shown below in Equations 1-6:

1 $$(CH_3)_2CHOH + \gamma \text{ ---> } (CH_3)_2CHOH^*$$

2 $$(CH_3)_2CHOH^* \text{ ---> } e^-_{sol} + (CH_3)_2CHOH^+$$

3 $$(CH_3)_2CHOH^+ \dashrightarrow H^+ + (CH_3)_2\dot{C}OH$$

4 $$(CH_3)_2\dot{C}OH + OH^- \dashrightarrow (CH_3)_2\dot{C}O^- + HOH$$

5 $$(CH_3)_2\dot{C}O^- + RCl \dashrightarrow (CH_3)_2CO + Cl^- + \dot{R}$$

6 $$\dot{R} + (CH_3)_2CHOH \dashrightarrow RH + (CH_3)_2\dot{C}OH$$

Generation of the α–hydroxy isopropyl radical from ionized isopropanol is shown in Equation 3. This radical undergoes an acid-base reaction in the alkaline solution in Equation 4, producing the acetone radical anion. This anion then transfers an electron to a PCB molecule (or other chlorinated hydrocarbon) in Equation 5 causing dechlorination. In Equation 6 it can be seen that the dechlorinated PCB radical stabilizes as a dechlorination daughter species by proton abstraction from the solvent, creating a new α-hydroxy isopropyl radical and initiating the chain reaction. This chain reaction results in the high G values reported[5,6]. Alkaline isopropanol has been the solvent of choice for organochlorine compound radiolysis studies since the pioneering work of Sherman[2] because of these high G values. Singh, et. al., have proposed treatment of PCB contaminated transformers using radiolysis in this solvent[6].

The PCBs however, are usually found in an oil matrix in actual wastes. It has been reported in at least one study that PCB radiolysis rates in oils are unacceptably low for use as a treatment technology[12]. This report contradicts that conclusion.

At the INEL the radiolysis of PCBs in neutral isopropanol was investigated over a period of several years[7,8,9] as a first step toward modeling more "real world" solvents. It was determined that the dechlorination chain reaction which occurs in alkaline isopropanol does not occur in neutral isopropanol[7]. Consequently PCB decomposition rates are about four orders of magnitude lower ($G= 0.1$ molecules $100\ eV^{-1}\ g^{-1}$). This is due to the fact that the α-hydroxy isopropyl radical produced by isopropanol radiolysis does not undergo an acid/base reaction in neutral solution to produce the acetone radical anion. The α–hydroxy isopropyl radical is apparently unable to participate in the chain-reaction dechlorination of PCBs[7,8].

However, in this system PCB decomposition by dechlorination still occurs. It is accompanied by the ingrowth of daughter congeners produced by sequential dechlorination. Similarly to radiolysis in alkaline isopropanol the predicted end product of complete dechlorination is biphenyl. Although dechlorination rates are much lower in neutral isopropanol than in alkaline isopropanol a 200 mgL^{-1} solution of PCB 200 was decomposed by an order of magnitude using amounts of radiation easily achievable in our system[7].

When the natural logarithm of the PCB concentration was plotted versus the absorbed dose for experiments in neutral isopropanol it was revealed that the reaction observed first-order kinetics. The slope of the line obtained is a reaction efficiency analogous to a rate constant. We called this slope the dose constant (d) since it was expressed in terms of reciprocal dose rather than time[8]. This dose constant was independant of initial PCB concentration and radiation dose rate in neutral isopropanol[8]. It was thus a valuable figure of merit in that system, and was used instead of the more traditional G value. The G value suffers from a concentration dependance which makes it impractical for comparing experiments with different initial PCB concentrations. Much of the discussion to follow would not be possible without adopting the use of the dose constant.

Dose constants were obtained for twenty-five PCB congeners in neutral isopropanol[9]. It was found that a general increase in dose constant occurred as the number of chlorine atoms on the molecule increased. However considerable variability existed among members of any selected homolog series. PCBs with the largest dose constants for their homolog series were para/meta substituted only. Apparently chlorine substitution in the ortho position decreased neutral isopropanol radiolysis efficiency. When the dose constants for our 25 congeners were plotted versus their LUMO energies a strong correlation was found[9]. The LUMO energies are those of Greaves[14] and were found to be lowest for congeners substituted in only the para and meta positions. These congeners, which decomposed quickly via radiolysis in neutral isopropanol, are the "planar" congeners. The lack of ortho substitution allows the two phenyl rings to achieve a nearly coplanar configuration and the extended conjugation which results is thought to lower the energy of the LUMO. Increasing chlorine substitution also leads to lower LUMO energies due to the electron withdrawing nature of the chlorine. Low LUMO energies lead to high dose constants (high radiolysis rates). Congeners with ortho chlorine substitution are restricted from free rotation around the phenyl-phenyl bond and the planar configuration is not easily adopted. They have higher LUMO energies. Ortho substituted congeners also had lower dose constants[9]. Since it is well known that captured electrons reside in the LUMO[15] these correlations strongly suggested that radiolytic PCB dechlorination in neutral isopropanol proceeds by electron capture. The source of these electrons is the interaction of gamma-rays with the isopropanol solvent, as shown in Equation 2. These radiolytically produced high-energy electrons are rapidly thermalized and become solvated in polar media[16]. They are then able to react as a very powerful chemical reducing agent.

It was confirmed that the solvated electron was the agent responsible for PCB dechlorination in neutral isopropanol via a series of scavenger experiments[8]. These experiments were performed by adding species known to have a high reaction rate with the suspected agent and observing the effect on PCB degradation. Reference to Buxton, et al.,[17] allowed the choice of appropriate scavenger species based upon their rates of reaction with various radicals. Although Buxton tabulated reaction rates in aqueous solution, extrapolation to isopropanol was valid since only relative rates were of concern.

The primary reactive agents produced by isopropanol radiolysis are solvated electrons, hydrogen atoms, hydroxyl radicals and the α–hydroxy isopropyl radical[16]. The highest yield products are the electron and α-hydroxy isopropyl radical, production of which is shown in Equations 2 and 3. The rapid reaction of hydrogen atoms and hydroxyl radicals with the isopropanol to form the α-hydroxy isopropyl radical predicts that their contribution to PCB decomposition is small[18]. The following scavenger experiment confirmed this prediction.

Nitrobenzene is a scavenger species with a diffusion limited rate of reaction with solvated electrons[17], and a high rate with the α-hydroxy isopropyl radical[19]. Benzene has a rate of reaction with the solvated electron three orders of magnitude less[17]. Both scavengers have similar reaction rates with the hydrogen atom and the hydroxyl radical[17]. The benzene rate with the alcohol radical is unknown. Dose constants for irradiated samples containing nitrobenzene were decreased by a factor of two[8], while benzene had no affect. These results indicated that hydrogen atoms and hydroxyl radicals do not have a significant role in the radiolysis of PCBs in neutral isopropanol. However the experiment was insufficient to permit a choice between the solvated electron and the alcohol radical.

Sulfur hexafluoride was chosen as an electron scavenger[8]. It is well known that sulfur hexafluoride has a high rate of reaction with electrons. It is believed to have little affinity for the α-hydroxy isopropyl radical based upon analogy with it's known rate for methyl radicals[20]. When experiments were sparged with sulfur hexafluoride the dose constant was reduced by a factor of five. These results, as well as the trends exhibited with PCB LUMO energy, confirmed that the solvated electron was the primary agent of PCB dechlorination in irradiated neutral isopropanol. However, the sulfur hexafluoride experiment showed that even in the suppossed absence of electrons a small amount of decomposition still occured. This may be due to competition for the electrons with the scavenger by PCBs, however minor participation by the α-hydroxy isopropyl radical through electron transfer can not be discounted[8].

Based upon this mechanism the expected products of dissociative electron capture by PCBs in isopropanol are daughter PCB congeners of decreased chlorine content and free chloride ion. Daughter PCBs did grow in to the irradiated neutral isopropanol solution with increasing absorbed dose[7,8]. The increase in free chloride ion with absorbed dose for irradiated solutions was linear, athough substoichiometric[8]. Carbon and chlorine mass balances showed that not all the initial PCB mass was accounted for as these products. Mass balance recoveries for both carbon and chlorine were within a few percent of each other[8]. This was considered an indication that an unidentified product contained both the carbon and the chlorine. Additionally, irradiation of a ^{14}C labelled congener showned that 100% of the carbon activity remained in solution following irradiation[9]. These data suggested that unidentified semivolatile compounds were being generated. This was confirmed by mass spectrometric results which identifed peaks having a retention time greater than that of the original PCB and which were not attributable to dechlorination daughters[9]. These compounds were identified by a combination of mass spectrometry and derivatization techniques as solvent-PCB adducts[9]. They are probably formed by the pathway shown in Equation 7:

7 $$\dot{R} + (CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CROH$$

The contribution of these adducts to the mass balance could not be evaluated by analytical chemistry due to the lack of appropriate calibration standards. However, when adduct formation was suppressed by nitrobenzene scavenging of the α-hydroxy isopropyl radical stoichiometric dechlorination occurred[8]. Similarly, sparging of solutions with nitrous oxide prior to irradiation, which enhances the alcohol radical concentration via Equations 8 and 9[19], enhanced the production of adducts[8]. Thus it was concluded that PCB decomposition via radiolysis in neutral isopropanol was fully explained by a combination of reductive dechlorination by electron capture and formation of a series of solvent-PCB adducts. It is known that these adducts are also susceptible to reductive dechlorination[8].

8 $$N_2O + e^-_{sol} \longrightarrow N_2 + \dot{O}^-$$

9 $$\dot{O}^- + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + OH^-$$

The results of these isopropanol studies have important implications for a PCB waste treatment process. The possibility of in-situ PCB treatment is obvious. The penetrating nature of the gamma-rays is evident in that the samples used for experimentation were separated from the fuel by the fuel cladding, a layer of water, the steel wall of the dry tube, the steel sample cannister and the glass walls of the sample vial[7]. Thus it is possible to remotely treat PCB containing articals. Also, it is evident that the PCBs were selectively attacked in the presence of the solvent. Further, the attack was reductive. This is an important consideration because the major objection concerning the currently approved PCB treatment of incineration is centered on the generation of small amounts of the toxic oxidative products dioxin and dibenzofuran. These compounds are not generated in a reductive process.

Following the neutral isopropanol study an investigation of PCB radiation chemistry in nonpolar solvents was begun at INEL as a next step toward understanding PCB radiolysis in oils[21]. Issoctane was selected as an oil surrogate due to its improved amenability to analytical methods. The yields of various radicals from irradiated hydrocarbons have been studied[16] and they are similar. Those radicals are hydrogen atoms, alkane radicals and the quasi-free electron. The individual yields vary only slightly so isooctane is a reasonable surrogate for many commercially avaliable oils.

As in isopropanol, PCB degradation was found to occur at reasonable rates, and to observe first-order kinetics[21]. A plot of the natural logarithm of PCB 200 concentration in isooctane versus absorbed dose is shown in Figure 1. Figure 2 shows PCB 200 daughter curves for typical data. These results are completely analagous to those in neutral isopropanol and immediately suggested a similar mechanism.

When the benzene/nitrobenzene scavenger experiment was repeated on isooctane solutions of PCBs it was determined that the hydrogen atom was again not a significant contributor to degradation[21]. Sulfur hexafluoride sparging significantly reduced the decomposition of PCBs in isooctane, implicating the electron in this system too.

Oxygen is a known electron scavenger[16] and many researchers conscientiously remove it from their systems prior to irradiation to study electron promoted mechanisms[4,5,6]. Nitrogen sparging (to remove oxygen) increased the degradation rate while oxygen sparging decreased the degradation rate of PCBs in isooctane[21]. This is consistant with a mechanism based upon electron capture.

Despite the obvious similarities of PCB radiolysis in isooctane with that in isopropanol the dose constant/LUMO energy correlation was not as obvious in isooctane. Further, the dose constants found to be dependant on initial PCB concentration in isooctane[21]. Thus congener dose constants were measured at identical initial concentrations for comparison and the dose constant lost its advantage over the G value as a figure of merit in the isooctane system. It was demonstrated that the rate of individual congener decomposition was actually slightly higher in isooctane than in isopropanol[21]. This was explained by isopropanol competition for the available electrons in that solvent. Isooctane has no measurable capture rate for electrons.

A mass balance anlysis of the PCB carbon and chlorine in isooctane solution following irradiation showed that a significant chlorine deficit occurred, and that this deficit became greater with increasing dose[21]. No significant free chloride ion was measured in the irradiated isooctane. The only products found were

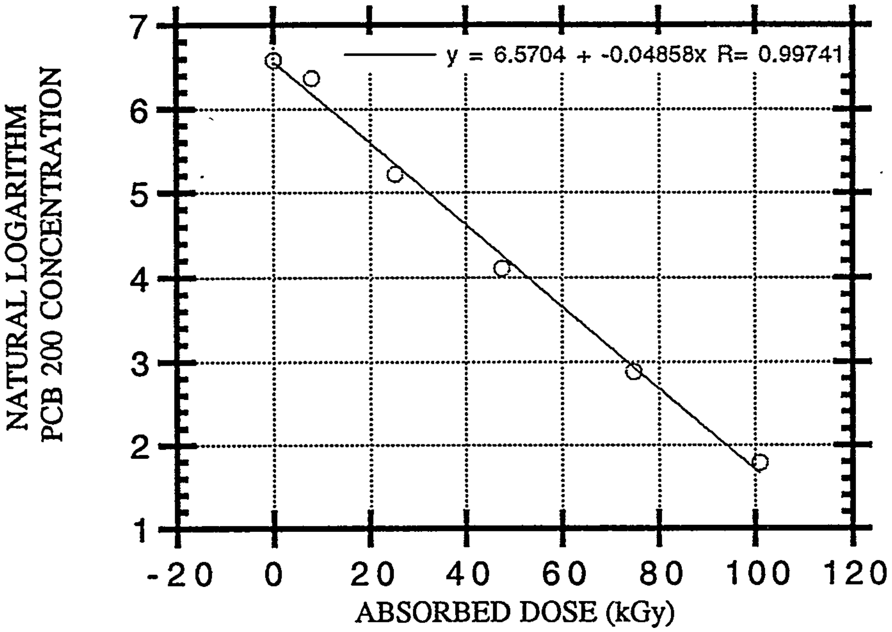


FIGURE 1. The natural logarithm of PCB 200 concentration versus absorbed dose. The initial concentration was 730 mgL^{-1}.

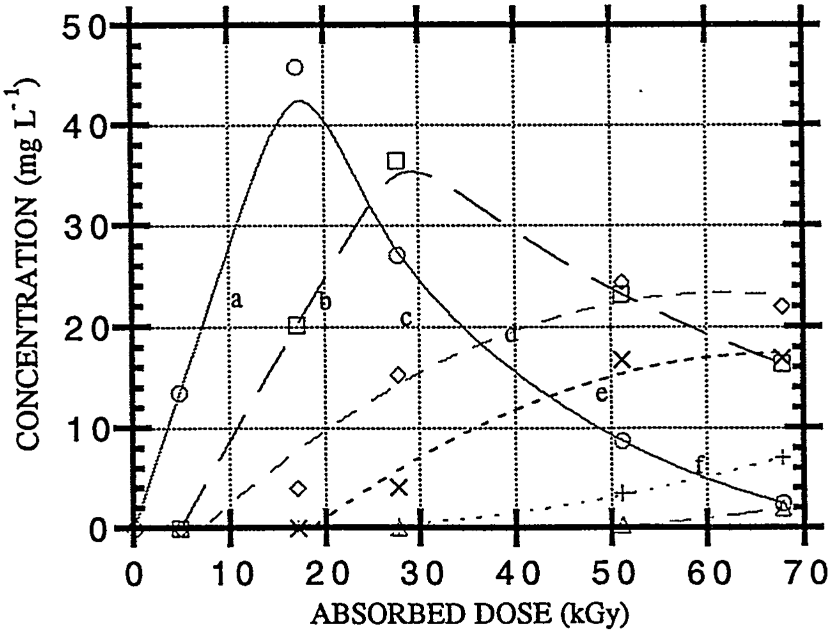


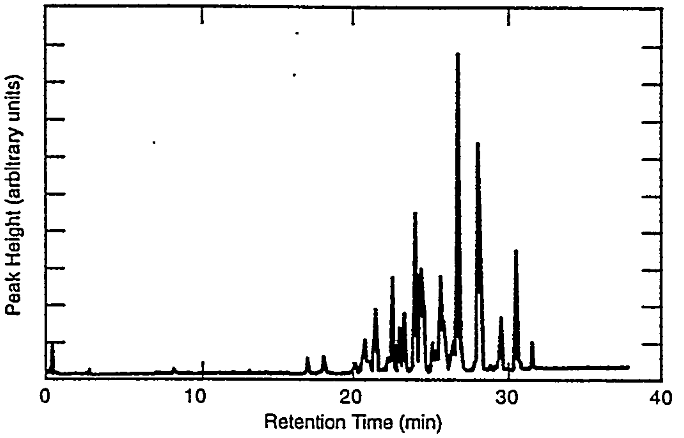
FIGURE 2. Production of dechlorination product PCBs from irradiated PCB 200. a; hepta-, b; hexa-, c; penta-, d; tetra-, e; tri-, and f; dichlorobiphenyls.

daughter PCBs and PCB-isooctane adducts. It was demonstrated that all the PCB carbon remained in the post-irradiation solutions using radiolabelled PCBs.

Despite the obvious differences in PCB radiolysis in isooctane and isopropanol the overall mechanism was believed to be similar and experiments were next performed in transformer oil[21], and hydraulic oil (unpublished). Shell Diala A transformer oil was spiked with the commercial PCB mixture Aroclor 1260. The solution was irradiated as previously for individual congeners in other solvents, and it was found that an absorbed dose of 229 kGy reduced the Aroclor 1260 concentration from 5000 to 1800 mgL^{-1} [21]. Electron capture detector (ECD) chromatograms for the pre-, and post irradiation samples are shown in Figure 3. These findings contradicted those of the only other known study concerning PCB radiolysis in electrical insulating oils. Webber[12] reported that no significant PCB decomposition occurred in "white insulating oils" even at high absorbed doses. The apparent contradiction may be explained by the relationship between dose constant and initial PCB concentration reported above for isooctane. Webber conducted most of his experiments at concentrations in excess of 10,000 mgL^{-1}. He was able to dechlorinate Aroclor 1260 in a single experiment performed at 40 mgL^{-1}.

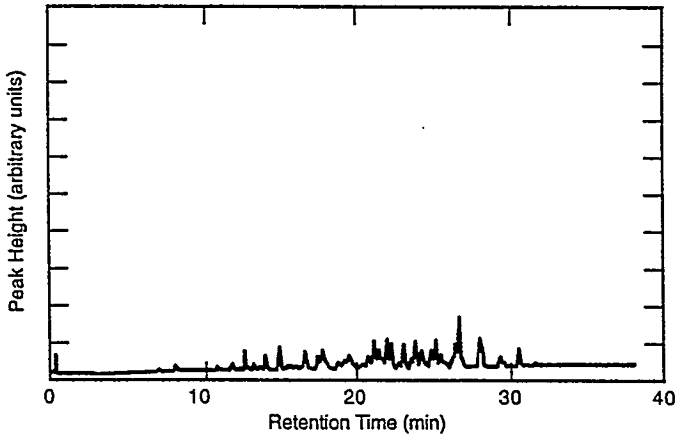
PCB radiolysis in hydraulic oils was a special concern at the INEL. Several "wastestreams" at INEL contain hydraulic oils which are both radiologically and PCB contaminated. Removal of the PCB componant would considerably decrease the regulatory constraints associated with handling these wastestreams. Harvest King hydraulic oil was spiked with 5000 mgL^{-1} Aroclor 1260 and irradiated to a maximum absorbed dose of 229 kGy. The Aroclor concentration was reduced to 520 mgL^{-1}. The ECD chromatograms are shown in Figure 4. This data has not been previously reported in the literature.

The Aroclor 1260 radiolysis experiments in transformer and hydraulic oil confirmed certain previous findings in isopropanol and isooctane. Inspection of the chromatograms in Figures 3 and 4 reveals that not only did significant PCB decomposition occur at moderate absorbed dose but also that daughter PCBs grew in to the irradiated solutions. These appear in the chromatograms as new peaks at lower retention times. The PCBs decomposed by dechlorination in industrial oils. When transformer[21] and hydraulic oils (unpublished data) were sparged with



5000 ppm Aroclor 1260 in Transformer Oil prior to irradiation

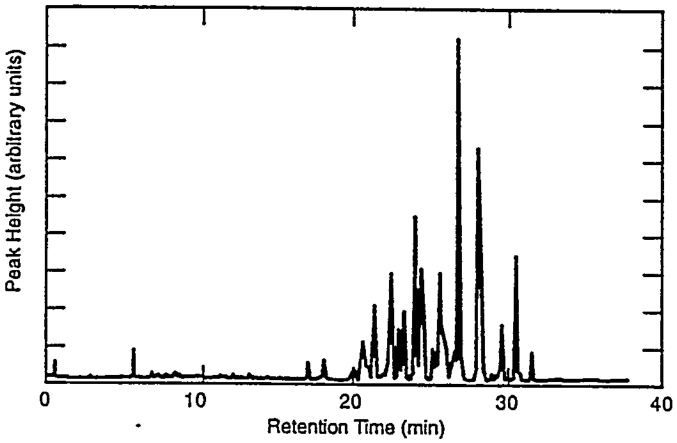
S1955157-1



1823 ppm remaining following 230 kGy absorbed dose

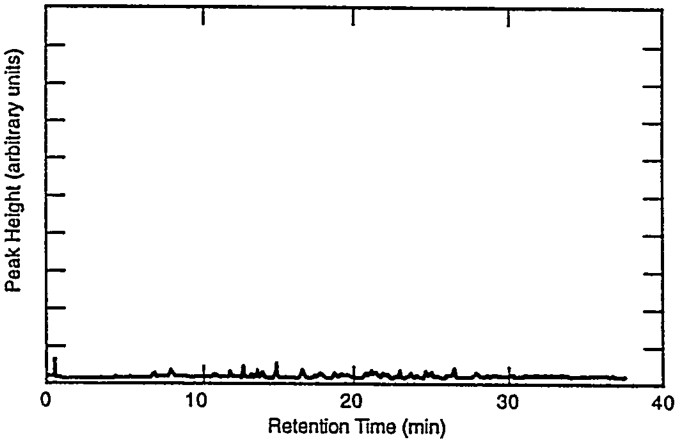
S1955157-2

FIGURE 3. Electron capture detector gas chromatograms for Aroclor 1260 decomposition in Shell Diala A transformer oil. The top chromatogram is before irradiation; the bottom is following 230 kGy absorbed dose.



5000 ppm Aroclor 1260 in Hydraulic Oil prior to irradiation

S1955024-1



566 ppm remaining following 230 kGy absorbed dose

S1955024-2

FIGURE 4. Electron capture detector gas chromatograms for Aroclor 1260 decomposition in Harvest King hydraulic oil. The top chromatogram is before irradiation,the bottom is following 230 kGy absorbed dose.

sulfur hexafluoride prior to irradiation the rate was suppressed to a similar extent as that reported for isooctane.

Further, the rate of PCB decomposition in hydraulic oil was much higher than in transformer oil. The finding that the rate is influenced by the type of oil has obvious implications for any treatment process based upon radiolysis.

EXPERIMENTAL METHODS

Irradiations

Samples were irradiated using gamma-rays from spent nuclear fuel at the ATR canal. A dry tube designed for experiment insertion allowed the samples to be lowered into a position surrounded by up to six fuel elements. The arrangement is shown in Figure 5. Dose rates varied with the age of the fuel and ranged from 30 $kGyhr^{-1}$ to 1 $kGyhr^{-1}$. A typical value during these experiments was 10 $kGyhr^{-1}$. Previous work has demonstrated that decomposition rates are not affected by dose rate changes in this range[9]. The average gamma-ray energy was 700 kev. The samples were contained in 3 mL glass vials sealed inside stainless steel capsules. A schematic of the sample containers is shown in Figure 6. The samples were radiologically clean following irradiation (excepting the original contamination in the treatability study samples). Isotope gamma-rays are not energetic enough to cause activation of the samples, and the multiple layers of containment prevented cross-contamination from the canal. Further details concerning the irradiation procedure may be found in Reference 7.

Absorbed doses to the samples were measured using the FWT-60 radiochromic film supplied by Far West Technology (Goleta, CA.). The film calibration has been previously discussed in detail[22]. Samples were irradiated to an increasing series of absorbed doses by varing their exposure time in the dry tube.

Analytical Methods

The treatability study samples were analyzed for Aroclor 1260 content using a commercial laboratory (Maxim Technologies, Inc., St. Louis, MO.). The laboratory

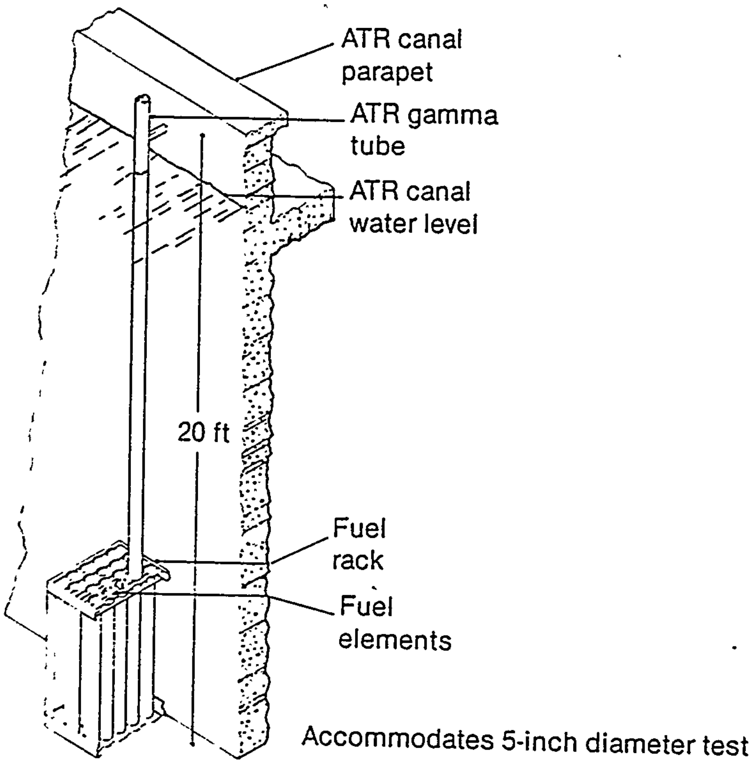


FIGURE 5. The ATR Gamma Facility, showing the dry tube extending from the canal surface into the spent fuel rack. The dry tube allows for experiment insertion into the high gamma-ray dose rates associated with the fuel.

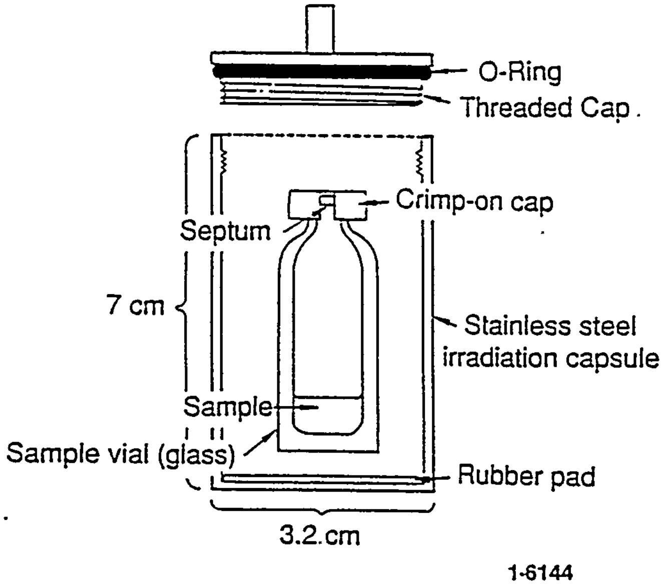


FIGURE 6. Schematic of the capsules which were used for experiment irradiations in the ATR canal gamma facility dry tube. The multiple layers of containment prevented cross-contamination of the samples but allowed for in-situ radiolysis of the PCBs.

performed a sulfuric acid digestion on the oils followed by hexane extraction of the PCBs. This fraction was then analyzed using electron capture detection gas chromatography. Their protocols may be found in Reference 23.

INEL Oil Wastestreams

The oils used in the treatability study were selected from wastestreams in storage at the INEL's Mixed Waste Storage Facility. These oils were known to be contaminated with Aroclor 1260 (a commercial formulation containing a mixture of several PCB congeners) and small amounts of ^{137}Cs. Five wastestreams were available. They are designated 610, 611, 612, and 613 from crane crankcases and 1002 from the TAN V tanks. Upon further characterization it was discovered that wastestream 610 contained a very low PCB concentration and it was not selected for use in the study. The wastestream 1002 was found to be mostly aqueous and it too was not selected for use. The remaining wastestreams were the subject of the treatability study. Table 1 below shows their characterization:

Table 1. Characterization of wastestreams selected for treatability study.

Wastestream	**Aroclor ppm**	**^{137}Cs pCimL^{-1}**	**Comments**
611	98	1.4E-1	oil contains sediment, possible benzene, and unidentified peaks detectable by ECD
612	44	1.4E-1	oil contains sediment
613	89	1.4E-1	oil visually clear, possible lead contamination

TREATABILITY STUDY

Based upon the research described in the Introduction of this report a series of irradiations was designed to demonstrate the feasibility of decontamination of PCB contaminated oils using gamma-ray radiolysis. Three radiologically contaminated PCB oils in storage at the INEL Mixed Waste Storage Facility were the subject of this treatability study. These oils are described in the Experiments section of this report. They are designated wastestreams 611, 612 and 613. These oils are known to contain the impurities expected in any used industrial oil. It was unknown to what extent these impurities might interfere with the PCB electron capture reaction upon which successful treatment depended. A preliminary irradiation was performed with a maximum absorbed dose of 183 kGy. A decrease in the Aroclor 1260 concentration was found in all three waste streams, with wastestream 613 showing the most favorable results. It's Aroclor 1260 concentration was decreased by a factor of two. Dose constants are not reported here for this initial irradiation because the limited amount of decomposition does not provide for reasonable uncertainties to be calculated.

A second irradiation to approximately 760 kGy was performed on the three wastestreams to generate the dose constants required to achieve the treatment standard. The absorbed doses and corresponding Aroclor 1260 concentrations for the irradiation of these wastestreams are shown in Table 2.

TABLE 2. Second irradiation results: The radiolytic destruction of Aroclor 1260 in INEL PCB Waste Streams.

	Aroclor ($mgkg^{-1}$)		
Absorbed Dose (kGy)	611	612	613
0	95	45	92
106	84	33	66
185	69	28	36
285	47	23	24
483	18	13	7
757	8	8	2

It can be seen from these data that the treatment standard of 2 $mgkg^{-1}$ was met in the second irradiation for wastestream 613 at an absorbed dose of 757 kGy. The treatment standard of 2 $mgkg^{-1}$ is also the detection limit for the laboratory[23]. The natural logarithm of these concentrations was plotted against the absorbed dose for each wastestream. The resulting dose constants were: 611 = 0.0035 +/- 0.0005 kGy^{-1}; 612 = 0.0023 +/- 0.0002 kGy^{-1}; 613 = 0.0052 +/- 0.0004 kGy^{-1}. The plots are shown in Figures 7 through 9. The corresponding ECD chromatograms for the untreated oil, and following irradiation to 757 kGy are shown in Figures 10 through 12.

The dose constants determined from the second irradiation were used to calculate the absorbed doses required to achieve the 2 $mgkg^{-1}$ goal for wastestreams 611 and 612. The calculation used was the standard first-order rate law:

$$C = C_0 e^{-dt} \tag{10}$$

where C is the treatment standard of 2 $mgkg^{-1}$, C_0 is the initial Aroclor concentration of the wastestream, d is the dose constant and t is the absorbed dose (rather than time). The predicted absorbed doses required were determined to be 1100 kGy for wastestream 611 and 1350 kGy for wastestream 612.

An third and final irradiation was performed on all three wastestreams to a maximum absorbed dose of 2242 kGy. Successful completion of the treatment standard was achieved at 1069 kGy for all three wastestreams. This data is shown in Table 3.

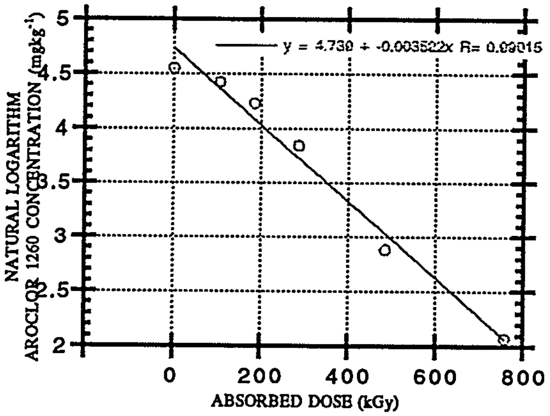


FIGURE 7. Dose constant plot for the second irradiation of wastestream 611.

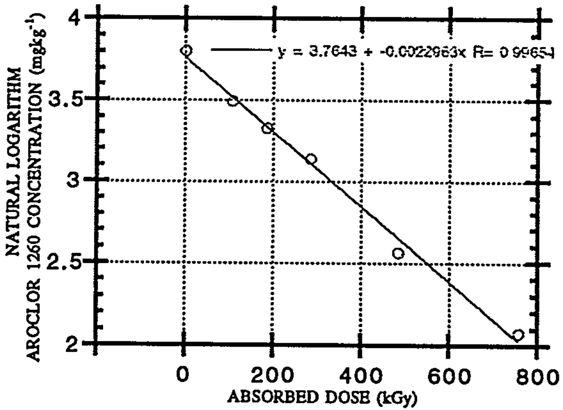


FIGURE 8. Dose constant plot for the second irradiation of wastestream 612.

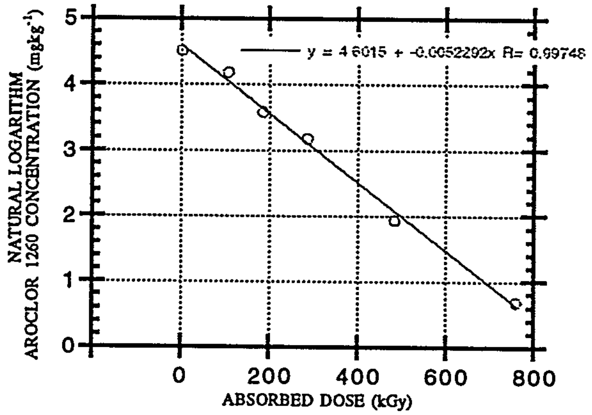


FIGURE 9. Dose constant plot for the second irradiation of wastestream 613.

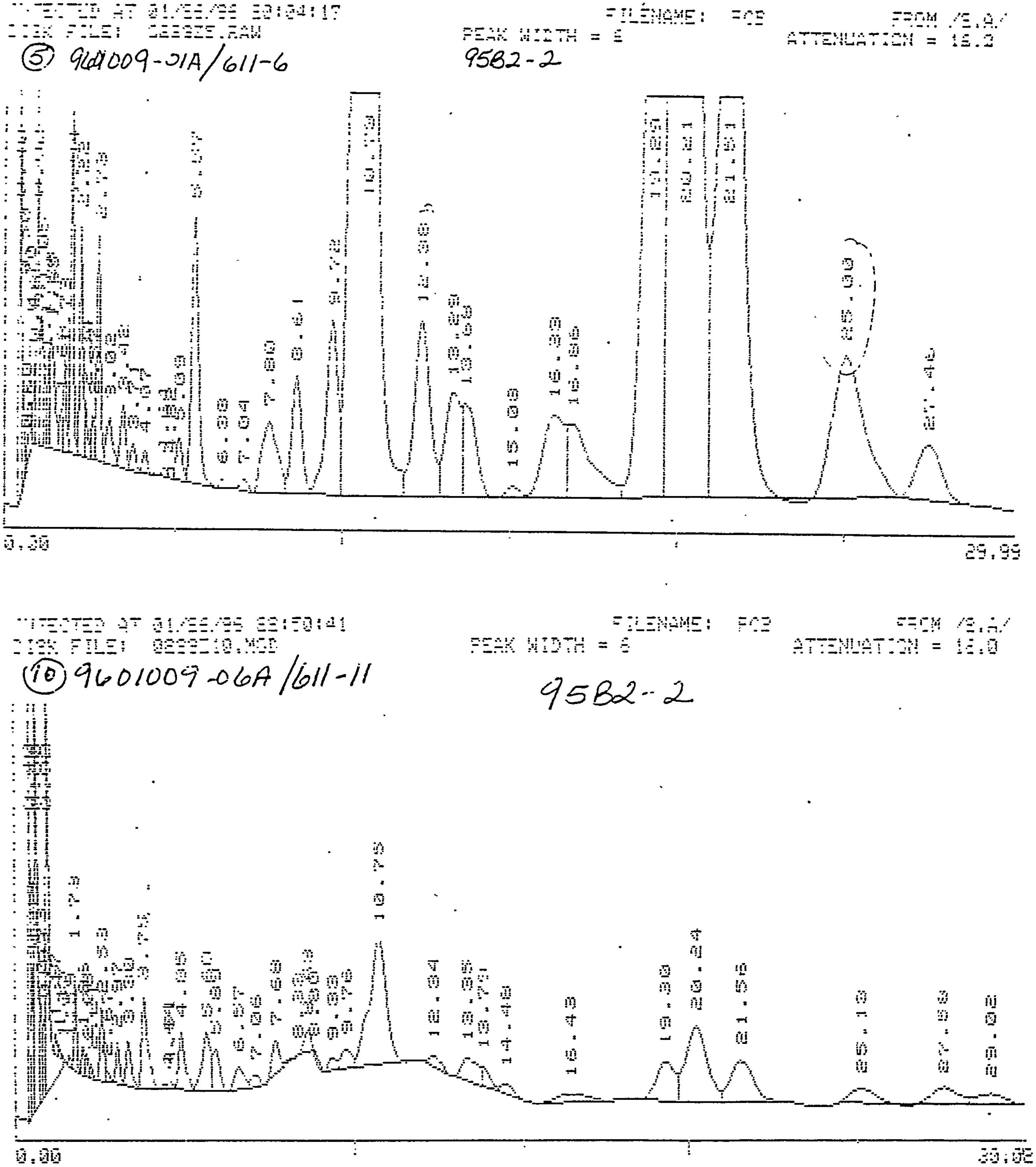


FIGURE 10. Electron capture detector gas chromatograms for the second irradiation of wastestream 611. The top chromatogram is for the pre-irradiation sample; the bottom is following 757 kGy absorbed dose.

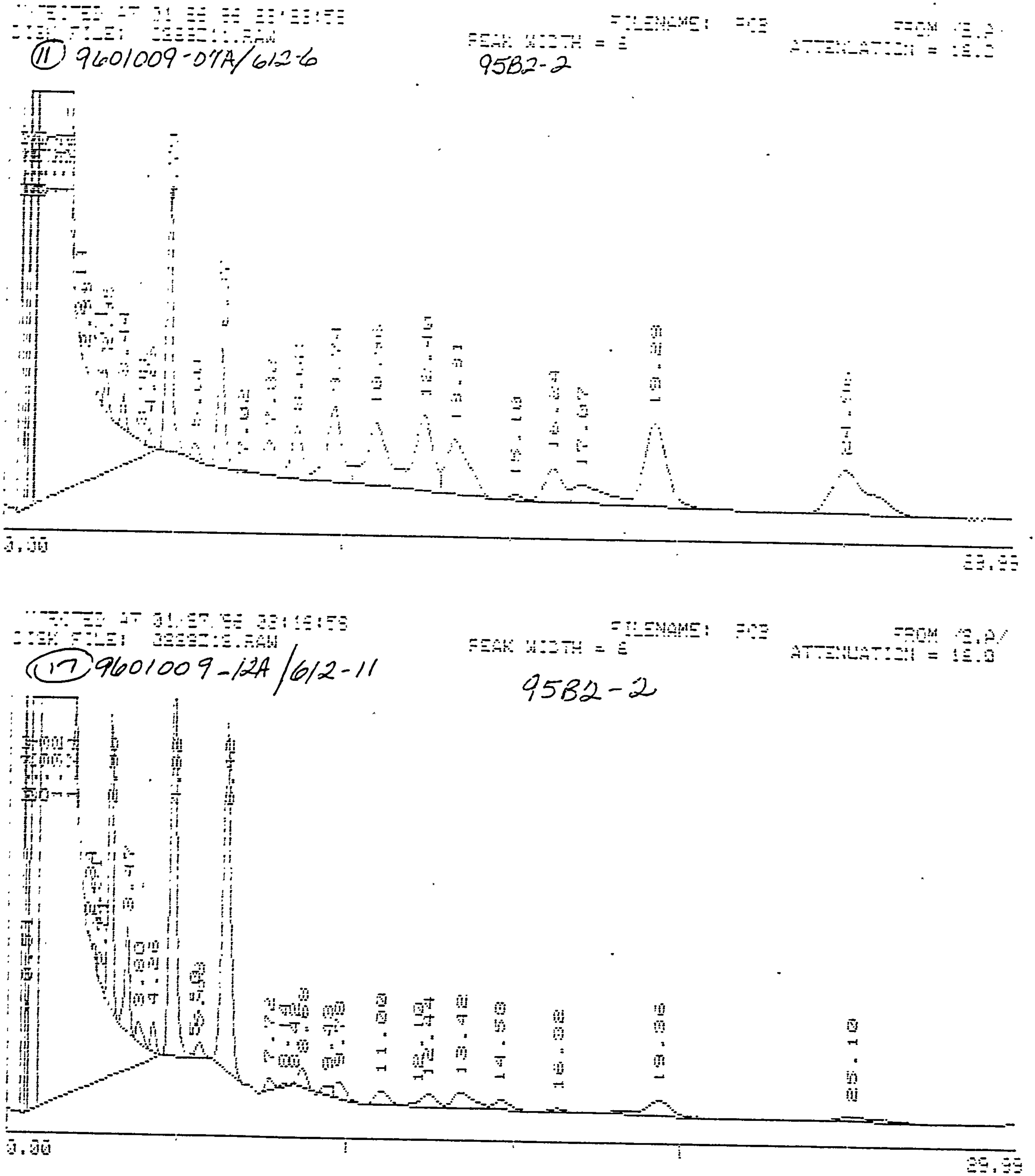


FIGURE 11. Electron capture detector gas chromatograms for the second irradiation of wastestream 612. The top chromatogram is for the pre-irradiation sample; the bottom is following 757 kGy absorbed dose.

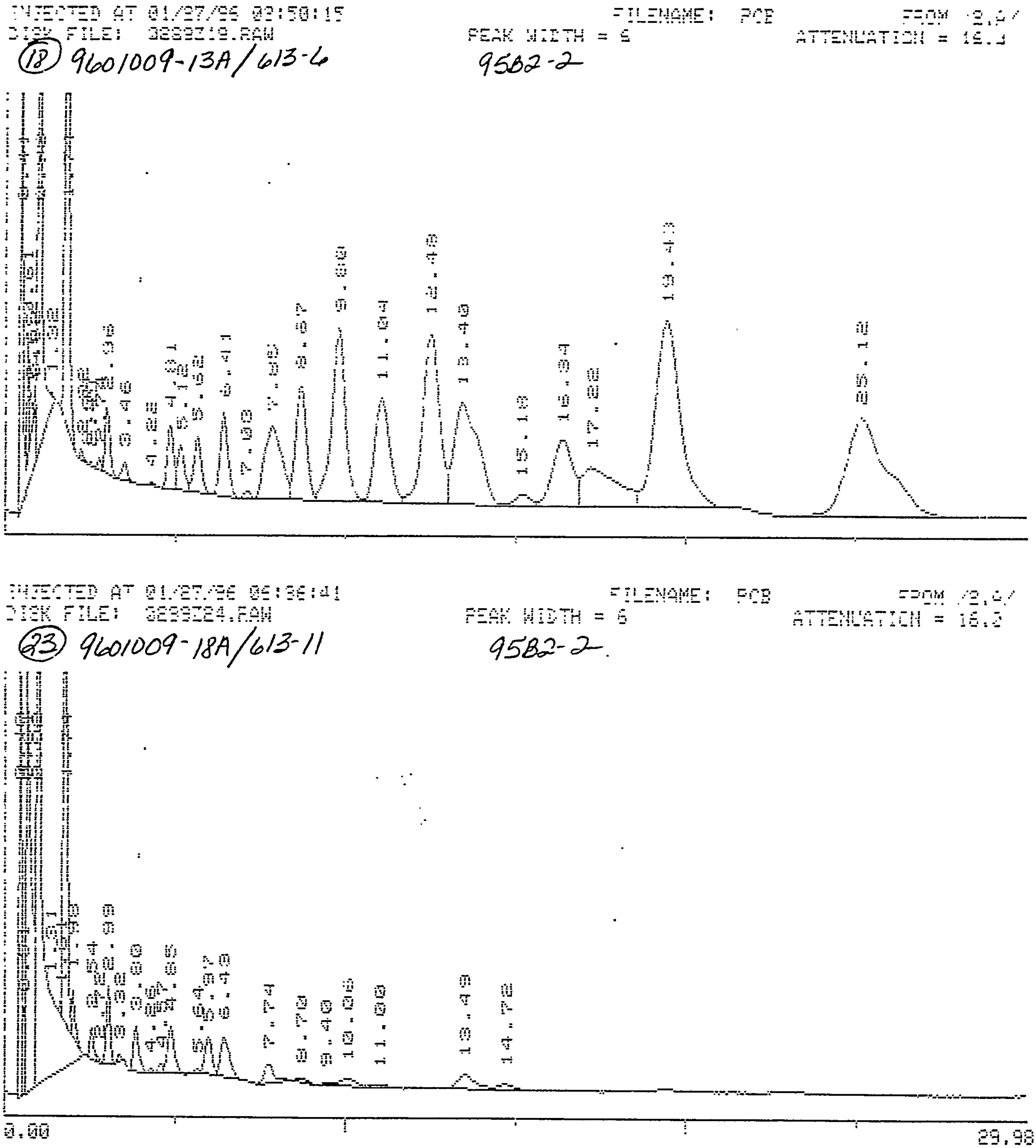


FIGURE 12. Electron capture detector gas chromatograms for the second irradiation of wastestream 613. The top chromatogram is for the pre-irradiation sample; the bottom is following 757 kGy absorbed dose.

TABLE 3. Final irradiation results: The radiolytic destruction of Aroclor 1260 in INEL PCB wastestreams.

Absorbed Dose (kGy)	Aroclor ($mgkg^{-1}$) 611	612	613
0	90	34	81
178	59	26	40
677	10	10	2
1069	2	2	2
1851	2	2	2
2242	2	2	2

Plots of the natural logarithm of the Aroclor concentrations versus absorbed dose are linear prior to achieving the detection limit and the slopes are in excellent agreement with those measured for the second irradiation. These plots are shown in Figures 13-15. The corresponding ECD chromatograms are shown in Figures 16-18.

CONCLUSIONS

The EPA mandated treatment standard of 2 $mgkg^{-1}$ was successfully met for the three INEL PCB wastestreams using gamma-ray radiolysis. The gamma-ray source was spent fuel at the ATR.

It is known from previous research that the radiolytic decomposition of PCBs in oils proceeds by electron capture resulting in dechlorination. This was demonstrated both by scavenger experiments in which PCB decomposition was suppressed by addition of electron capturing agents and by the measured production of less chlorinated congeners. The kinetics of the system is understood well enough from these earlier studies for adequate prediction of the absorbed doses required for adequate treatment of the INEL wastestreams. The required doses were within the range which were easily delivered using ATR spent fuel. These doses are also within the range which may be delivered using industrial isotope sources and accelerators.

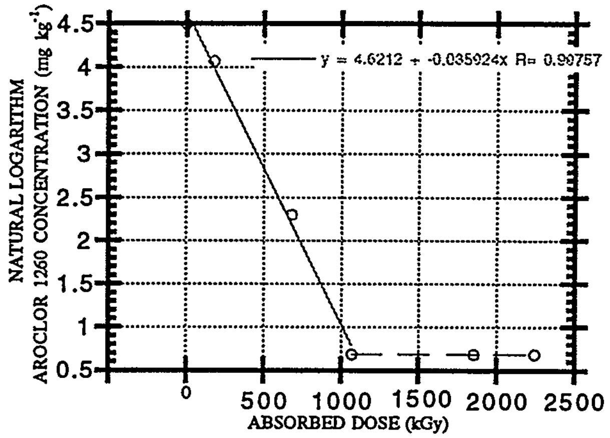


FIGURE 13. Dose constant plot for the third irradiation of wastestream 611.

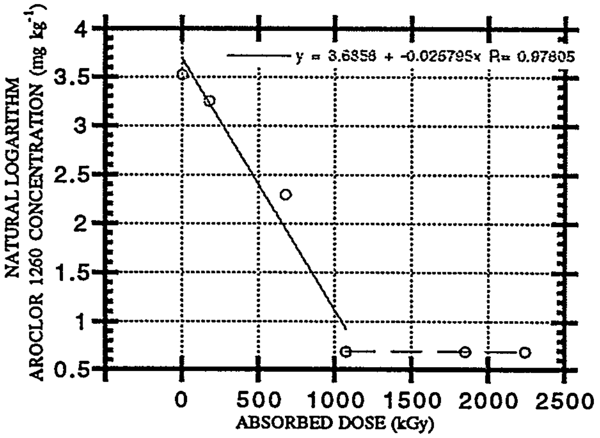


FIGURE 14. Dose constant plot for the third irradiation of wastestream 612.

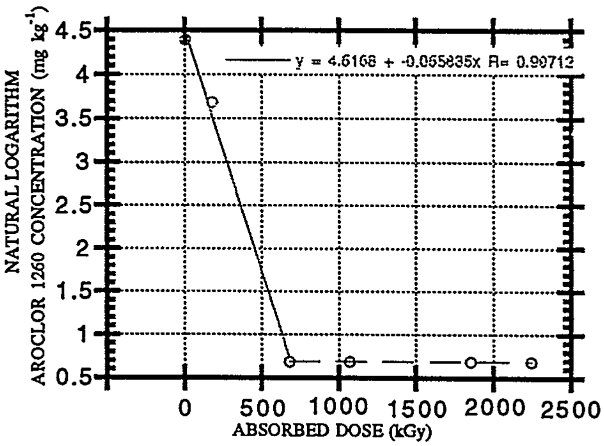


FIGURE 15. Dose constant plot for the third irradiation of wastestream 613.

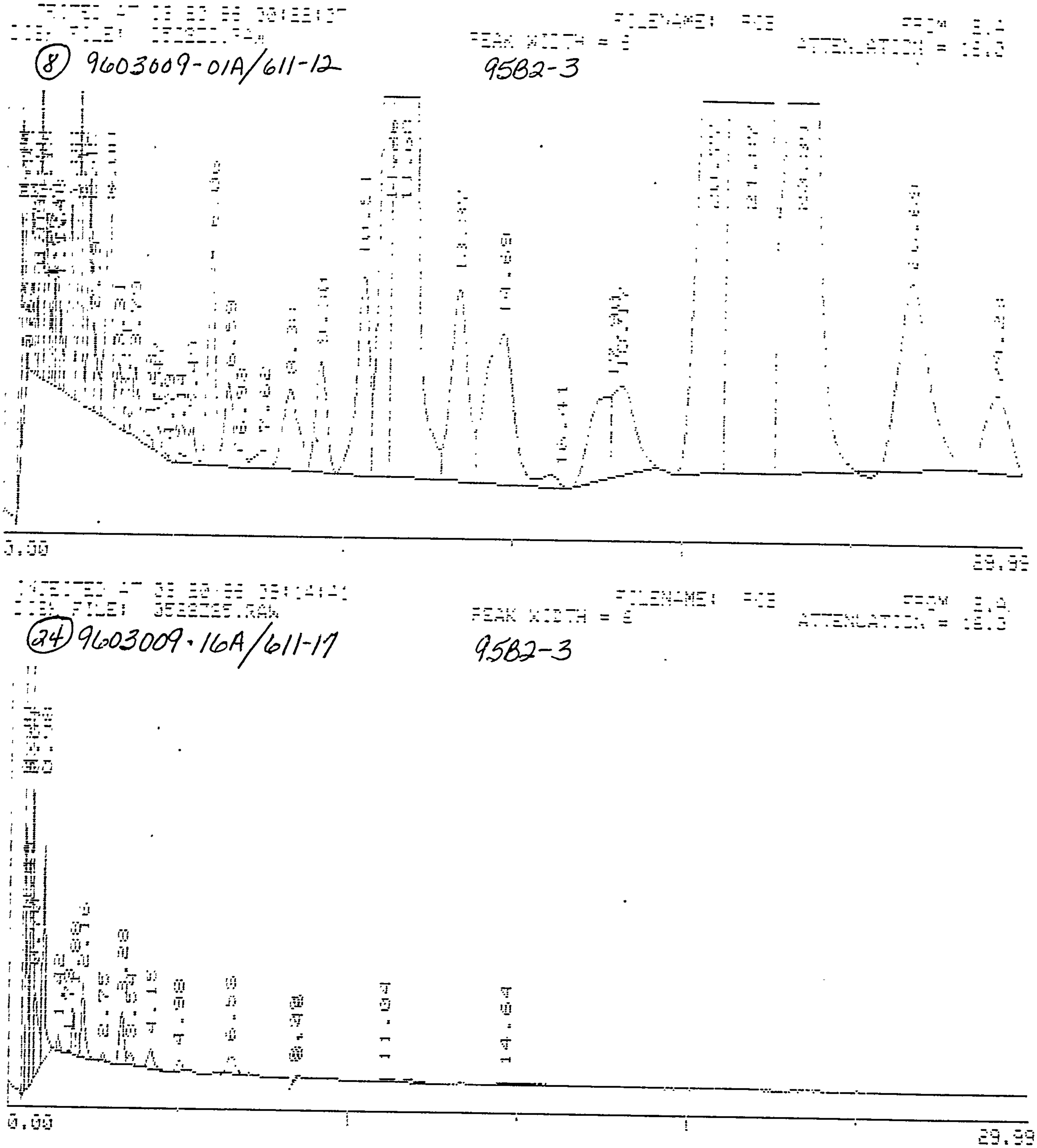
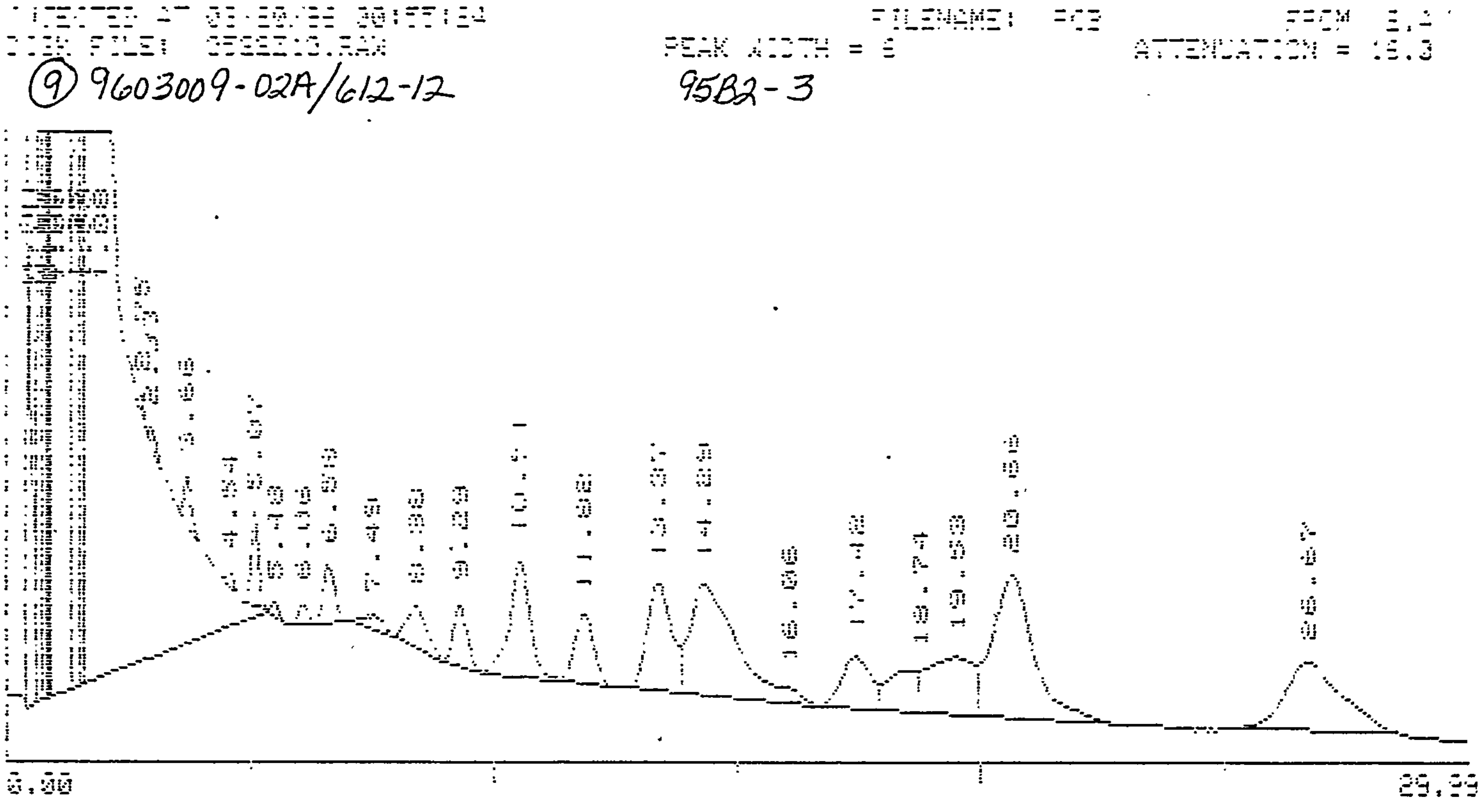


FIGURE 16. Electron capture detector gas chromatograms for the third irradiation of wastestream 611. The top chromatograph is for the pre-irradiation sample; the bottom is following 1851 kGy absorbed dose. The treatment standard of 2 $mgkg^{-1}$ has been achieved.



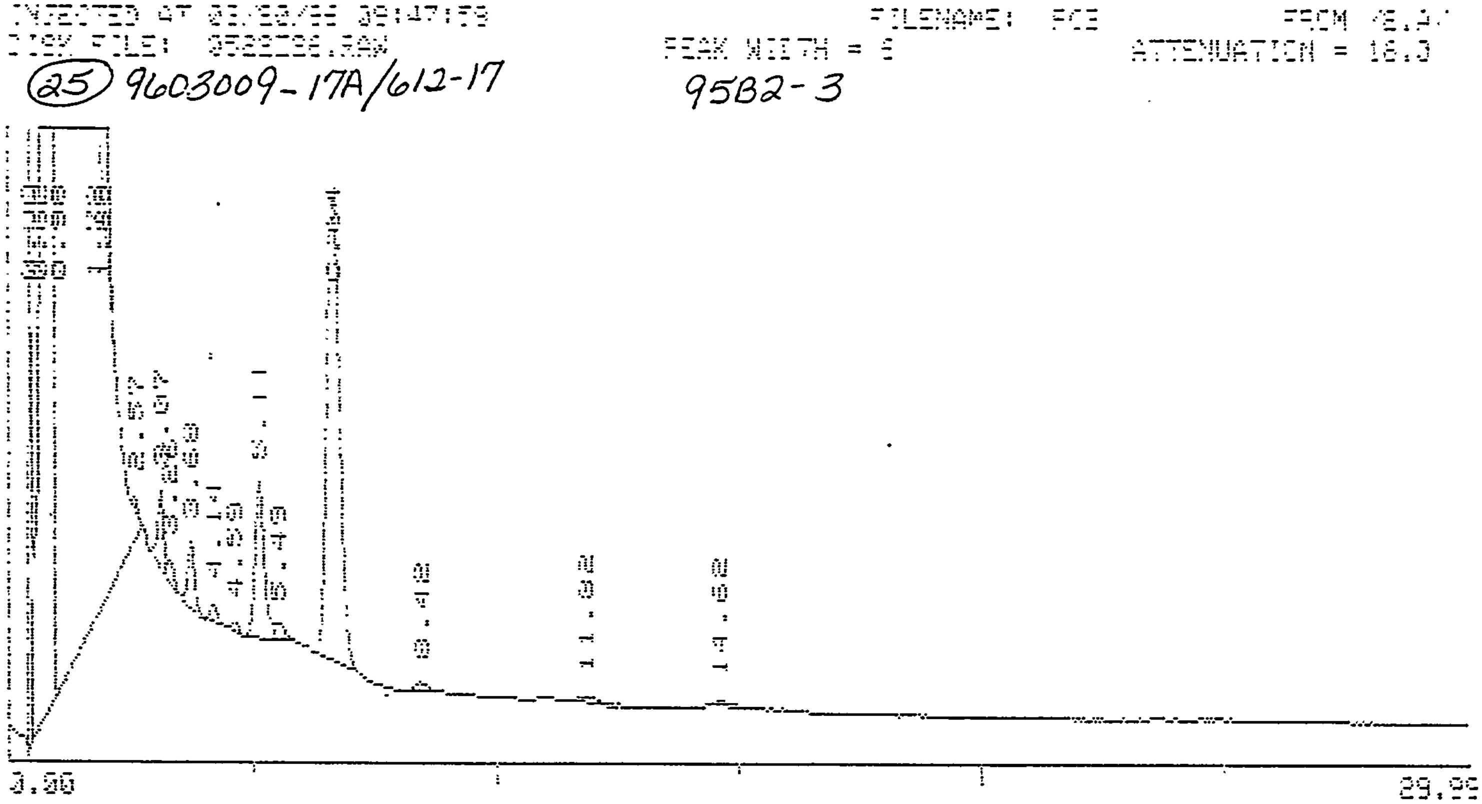


FIGURE 17. Electron capture detector gas chromatograms for the third irradiation of wastestream 612. The top chromatograph is for the pre-irradiation sample; the bottom is following 1851 kGy absorbed dose. The treatment standard of 2 mgkg^{-1} has been achieved.

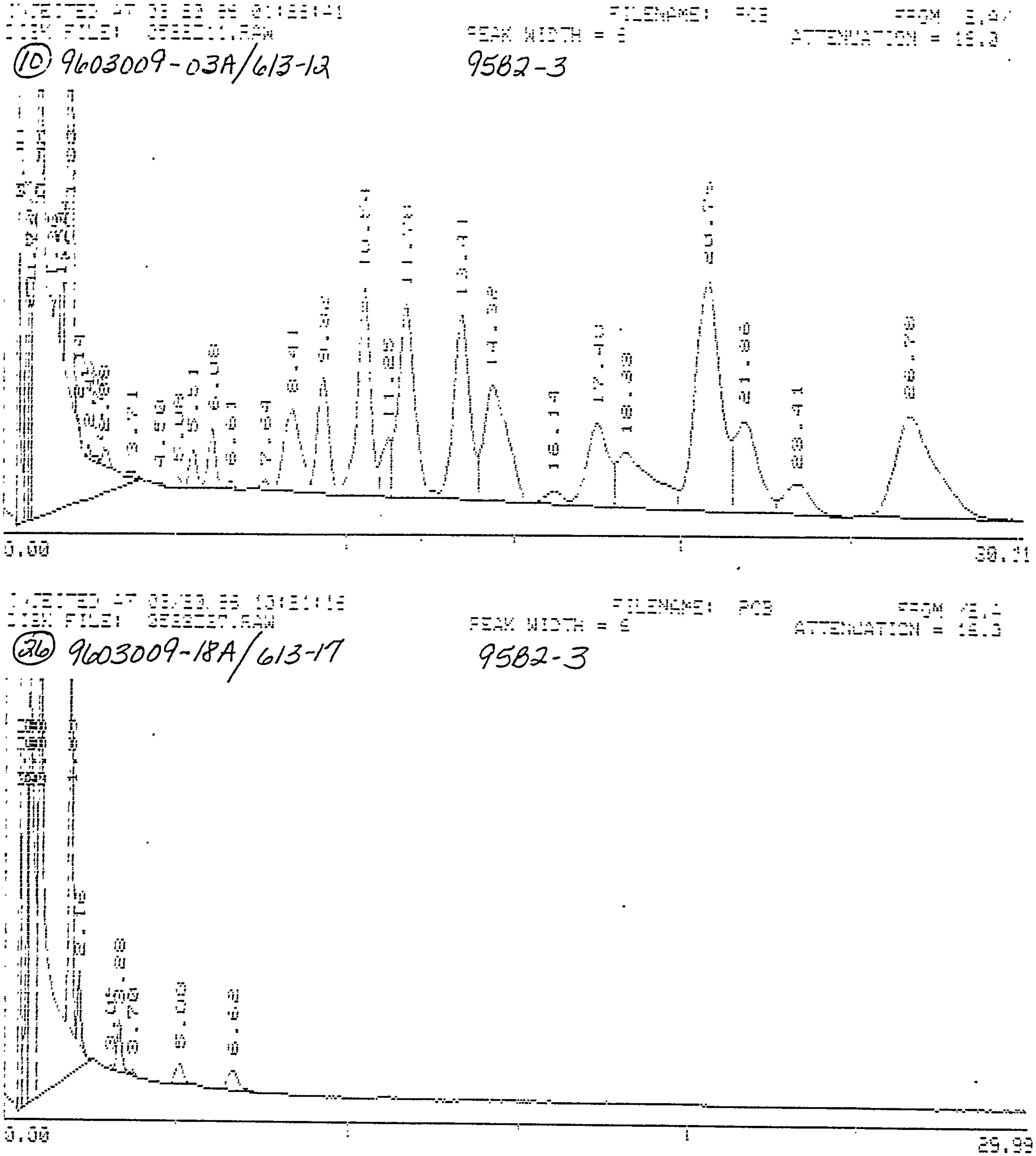


FIGURE 18. Electron capture detector gas chromatograms for the third irradiation of wastestream 613. The top chromatograph is for the pre-irradiation sample; the bottom is following 1069 kGy absorbed dose. The treatment standard of 2 mgkg^{-1} has been achieved.

13 J.H. Exner, Detoxification of Hazardous Waste, Ann Arbor Science, Ann Arbor, 1992.

14 J. Greaves, E. Harvey, W.G. MacIntyre, *Correlation between Electron Capture Negative Chemical Ionization Mass Spectrometric Fragmentation and Calculated Internal Energies for Polychlorinated Biphenyls,* **J. Amer. Soc. Mass. Spectrom.**, 5, 44, 1987.

15 P. Kebarle, S. Chowdury, *Electron Affinities and Electron Transfer Reactions,* **Chem. Rev.**, 87, 513, 1987.

16 J.W.T. Spinks, R.J. Woods, Introduction to Radiation Chemistry, 3rd., Wiley Interscience, New York, 1990.

17 G.V. Buxton, C.L., Greenstock, W.P. Helman, A.B. Ross, *Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (OH/O-) in Aqueous Solution,* **J. Phys. Chem. Ref. Data**, 17, 513, 1988.

18 M. Simic, P. Neta, E. Hayon, *Pulse Radiolysis Studies of Alcohols in Aqueous Solution,* **J. Phys. Chem.**, 73, 3794, 1969.

19 V. Jagannadham, Steenken, S., *One-electron Reduction of Nitrobenzene by α-hydroxy Alkyl Radical via Addition/Elimination, an Example of an Organic Intersphere Electron-Transfer Reaction.* **J. Am. Chem. Soc.**, 106, 6542, 1984.

20 D.W. Johnson, G.A. Salmon, *Reaction of Hydroxylmethyl Radicals with some Solutes in Methanol,* **Faraday**, 71, 446, 1979.

21 R.E. Arbon, B.J. Mincher, W.B. Knighton, *γ-ray Destruction of PCBs in Isooctane and Transformer Oil,* **Environ. Sci. Technol.**, in press.

22 B.J. Mincher, M.K. Zaidi, *Calibration of Far West Technology (FWT-60) Radiochromic Dye Dosemeters,* **Radiat. Protect. Dosimetry**, 47, 571, 1993.

23 Maxim Technologies Data Package Report ER-TOS-310, 1996.

APPENDIX A
INEL Analytical Laboratory
Supplementary Data

INEL Analytical Laboratory Supplemental Data

INEL Analytical Results

The Aroclor 1260 analytical results used in this study were generated by the commercial laboratory. This was necessary to provide independant confirmation of the results and to satisfy EPA requirements for the use of a CLP certified laboratory. The same analyses were run at INEL for improved turn-around time on the data necessary for experimental planning. The INEL laboratory used a modified version of EPA Method 8080. The gas chromatographic parameters are shown in Table 1. The analyses were preceeded by the same sulfuric acid digestion and hexane extraction cleanup procedure used by the commercial laboratory. The INEL results are similar to, but not identical to the commercial results due to different column types, temperature programs and integration techniques. The INEL laboratory did not achieve a detection limit of 2 mgkg^{-1}, however there was no neccessity to do so for the purposes for which those samples were analyzed. It must be noted that these results were generated for experimental planning purposes only. For legal purposes the commercial laboratory results take precedence.

Table 1. INEL GC Parameters for Aroclor 1260 Analyses.

Hewlett Packard 5890 Series II GC with ECD
Hewlett Packard 7673 autosampler
column: DB-1701, 30m x 0.32 mm
carrier flow: 7.5 mL min^{-1} helium
makeup gas: 45 mL min^{-1} 95% argon, 5% methane
injection temperature: 60°C
temperature program: 10.0 °C min^{-1} to 180°C, hold 6 min., then 5.0°C min^{-1} to 250°C.

Table 2. INEL treatability study second irradiation results.

Absorbed Dose(kGy)	Aroclor (mgkg^{-1}) 611	612	613
0	83	33	86
106	73	32	56
185	66	23	83
285	57	23	49
483	52	18	29
757	30	10	1.7

Table 3. Final INEL treatability study irradiation results.

Absorbed Dose(kGy)	Aroclor (mgkg^{-1}) 611	612	613
0	83	33	86
178	48	19	52
677	15	8.4	9.8
1069		8.3	
1851	3.5	6.9	3.6
2242		5.5	4.0