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**TEST OF ELECTRON BEAM TECHNOLOGY ON SAVANNAH
RIVER LABORATORY LOW-ACTIVITY AQUEOUS WASTE
FOR DESTRUCTION OF BENZENE, BENZENE
DERIVATIVES, AND BACTERIA**

by

J. P. Bibler

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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**TEST OF ELECTRON BEAM TECHNOLOGY
ON SAVANNAH RIVER LABORATORY LOW-
ACTIVITY AQUEOUS WASTE FOR DESTRUCTION
OF BENZENE, BENZENE DERIVATIVES, AND
BACTERIA**

SCUREF Task Order #72

August 1993

Roger A. Dougal
Principal Investigator
Dept. of Electrical and Computer Engineering
University of South Carolina
Columbia, SC 29208

ABSTRACT

High energy radiation was studied as a means for destroying hazardous organic chemical wastes. Tests were conducted at bench scale with a ^{60}Co source, and at full scale (387 L/min) with a 1.5 MV electron beam source. Bench scale tests for both benzene and phenol included 32 permutations of water quality factors. For some water qualities, as much as 99.99% of benzene or 90% of phenol were removed by 775 krad of ^{60}Co irradiation. Full scale testing for destruction of benzene in a simulated waste-water mix showed loss of 97% of benzene following an 800 krad dose and 88% following a 500 krad dose. At these loss rates, approximately 5 Mrad of electron beam irradiation is required to reduce concentrations from 100 g L⁻¹ to drinking water quality (5 µg L⁻¹).

Since many waste streams are also inhabited by bacterial populations which may affect filtering operations, the effect of irradiation on those populations was also studied. ^{60}Co and electron beam irradiation were both lethal to the bacteria studied at irradiation levels far lower than were necessary to remove organic contaminants.

CONTENTS

This is the final project report on SCUREF Task Order #72. This report is divided into three sections. Two of the three sections were submitted by sub-contractors at Florida International University and at the University of Miami. The third section includes an evaluation of the test results by the Principal Investigator.

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SECTION IA

FINAL REPORT

**DESTRUCTION OF BENZENE IN SIMULATED LABORATORY WASTE USING HIGH
ENERGY ELECTRON BEAM IRRADIATION
(SCUREF Project Number D18642EE)**

William J. Cooper
Michael G. Nickelsen
Kaijun Lin

Drinking Water Research Center
Florida International University
Miami, FL 33199

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Introduction

High energy electron beam irradiation as a treatment unit process has potential application in many areas of water, wastewater and industrial waste treatment and in the area of toxic/hazardous waste disposal and site remediation (1-4). The ultimate disposal of toxic and hazardous organic chemicals is emerging as a priority in the search for new and innovative treatment technologies. By ultimate disposal we refer to the mineralization of the solutes of concern.

The factors regarded as important for developing a treatment process for the disposal of toxic and hazardous organic chemicals and for site remediation or industrial waste disposal are:

1. The process should be flow-through and be relatively rapid in the treatment.
2. The process should result in the formation of non-toxic reaction by-products, and with mineralization of the solutes as a goal.
3. The process should be able to treat water of differing quality, including the presence of suspended particles up to 10%.
4. The process should be able to treat soil contaminated with toxic organic chemicals.
5. The process equipment should be transportable so that it can be taken to the problem or used for on-site treatability studies.
6. The equipment should be rugged and operated relatively easily (automation is the goal) in the field.
7. The process should be capable of treating mixtures of organic chemicals and be relatively insensitive to solute concentration effects.
8. The process should also be configured in such a way so as to facilitate quality assurance that the process is working properly and according to the design specifications.

Statement of Objectives

The goal of this project was to determine whether electron beam technology could be a useful method for decontaminating organic compounds, specifically benzene, in Savannah River Laboratory (SRL) aqueous wastes. The specific objectives of the project were the following:

1. To determine the removal efficiency of benzene and phenol (and other benzene derivatives that are considered a potential problem), using high energy electron beam irradiation, from a simulated SRL low-activity waste stream. The experimental variables that were examined were solute (organic) concentration, radical scavengers, e.g. the nitrate ion, soap as dissolved organic carbon, phosphate ion and heavy metals s iron (II) and absorbed dose.
2. To elucidate the structure of reaction by-products at various doses using ^{60}Co γ irradiation using a simulated SRL low activity waste. This information assisted in determining reaction mechanisms and monitoring reaction by-products of the experiments that were conducted on a larger scale at the Electron Beam Research Facility.
3. To compare the results of removal efficiency obtained at the ^{60}Co source and the Electron Beam Research Facility.

Absorbed Dose Measurements

The amount of energy from the high energy electron beam that is absorbed by an irradiated material per unit mass is called dose, and is a measure of energy transfer to the irradiated material, in this case water, and capable of producing chemical or physical changes. A common unit of dose is the rad, defined as the energy absorption of 100 ergs per gram of material. The conversion of Grays, Gy, (an international standard dose unit) to rads is 1 Gy = 100 rads.

The amount of energy that is transferred to the irradiated material is not constant as the electrons penetrate deeper into the material. The maximum depth of penetration is directly proportional to the energy of the incident electrons and inversely proportional to the density of the material being irradiated. Thus the absorbed dose depends on the type and thickness of the material, the beam power, and the length of time the material is exposed to the electron beam.

In a continuously flowing aqueous system at the scale of our investigations, the absorbed dose can be estimated by measuring the temperature difference of the water stream before and after irradiation. The relationship is derived for pure water by the following:

$$1 \text{ rad} = 100 \text{ erg g}^{-1} \quad [1]$$

or

$$1 \text{ Mrad} = 1.0 \times 10^8 \text{ erg g}^{-1} \quad [2]$$

substituting in,

$$1 \text{ erg} = 2.39 \times 10^{-8} \text{ cal} \quad [3]$$

then

$$1 \text{ Mrad} = 2.39 \text{ cal g}^{-1} \quad [4]$$

converting to °C

$$1 \text{ Mrad} = 2.39 \text{ °C} \quad [5]$$

or,

$$d(t) = 418 \text{ krad } \text{°C}^{-1}. \quad [6]$$

Thus, the average absorbed dose (D_{AV}) in pure water is calculated using the equation:

$$D_{AV} = K(t_2 - t_1) \quad [7]$$

where, t_1 and t_2 are the before and after irradiation water temperature of the flowing stream in °C, respectively; and K is the constant of proportionality:

$$K = 418 \text{ krad } \text{°C}^{-1}. \quad [8]$$

Therefore, an increase 1°C in water temperature is equivalent to a dose of 418 krad in pure

water.

The measurement of $d(t)$ provides an estimate of absorbed dose in natural waters. A slight error results from the deviation from unit density (pure water) of the natural waters. The application of temperature difference to estimate the absorbed dose in irradiated sludges would result in an error which would increase with increasing solids content.

Aqueous Chemistry of High-Energy Electrons

The purpose of this section is to provide an brief overview of aqueous-based radiation chemistry. The studies reported in the literature relating to radiation chemistry have been conducted in pure aqueous solutions. The extrapolation of pure water data to natural waters is complicated by the presence of inorganic and organic matter (primarily humic substances) found in natural waters. These compounds may interact with the transient reactive species formed during irradiation and lead to side reactions not observed in pure water. An example is the reaction of hydroxyl radical with carbonate ions, similar to that observed in processes utilizing O_3 .

High-energy electron irradiation of pure water results in the formation of electronically excited states and/or free radicals along the path of the electron. 10^{-7} sec after the electron has passed through a solution the products that are present are (5-8):

Unlike photochemical reactions where one photon of light initiates one (molecular) reaction, a high energy electron is capable of initiating several thousand reactions as it dissipates its energy. The efficiency of conversion of a high energy electron, ionizing radiation, to a chemical process is defined as G (shown in brackets in Equation 9). G is the number of radicals, excited states, ions or other products, formed or lost in a system absorbing 100 eV of energy. Of the products formed in Equation 9, the most reactive are the oxidizing, hydroxyl radical ($OH\cdot$), and the reducing, aqueous electron (e_{aq}^-) and hydrogen atom ($H\cdot$). Thus, the chemistry of primary interest in the high energy electron irradiation process is that of these three species.

Aqueous Electron. The reactions of the aqueous electron, e_{aq}^- , with specific organic and inorganic compounds has been studied extensively (9-12). The e_{aq}^- is a powerful reducing reagent with an E^0 ($e_{aq}^- + H^+ \rightarrow \frac{1}{2}H_2$) of 2.77. The reactions of the e_{aq}^- are single electron transfer, the general form of which is:

The e_{aq}^- reacts with numerous organic chemicals and of particular interest to the field of toxic and hazardous wastes are the reactions with halogenated compounds. A generalized reaction is

shown below:

Thus, reactions involving the e_{aq}^- may result in the dechlorination of organohalogen compounds. Further reaction of the organic radical formed could result in the complete destruction of the compound and a specific example is given below in this section. The e_{aq}^- also reacts with other organic compounds and would contribute to the removal of these compounds from aqueous solutions. Examples of the rate constants of reactions of interest in this area are summarized later in this paper.

Hydrogen Atom. The reactions of $H\cdot$ with organic and inorganic compounds have also been summarized (13). The hydrogen atom accounts for approximately 10% of the total free radical concentration in irradiated water. The $H\cdot$ undergoes two general types of reactions with organic compounds, hydrogen addition and hydrogen abstraction.

An example of a typical addition reaction with an organic solute is that of benzene:

The second general reaction involving the $H\cdot$ is hydrogen abstraction:

Because of the relatively small second order reaction rate constant of $H\cdot$ with the common radical scavengers found in natural waters, it is possible that this transient radical may be important in removing some of the compounds of interest in site remediation. This treatment process is the only one in which this particular radical is formed.

Hydroxyl Radical. Reactions of the hydroxyl radical, $OH\cdot$, with inorganic and organic compounds has been well documented (13). Compilations of rate constants have been published (13-14). $OH\cdot$ can undergo several types of reactions with chemicals in aqueous solution. The types of reactions that are likely to occur are addition, hydrogen abstraction, electron transfer, and radical-radical recombination.

Addition reactions occur readily with aromatic and unsaturated aliphatic compounds. The resulting compounds are hydroxylated radicals:

Hydrogen abstraction occurs with saturated and many unsaturated molecules, e.g., aldehydes and ketones:

Inorganic electron transfer reactions are also common, and will occur when aqueous solutions are irradiated with high energy electrons. For example, reactions involving halogen ions (X^-) may occur:

The $X_2^\cdot$ can further react with organic molecules possibly forming halogenated organic compounds. The halogens of most interest are Cl^- and Br^- . Reactions of $OH^\cdot$ with Cl^- are unimportant in aqueous solutions above a pH of 2 and are of little concern in our application. In the experiments we have conducted to date we have no indication of the formation of any organobromine compounds.

Hydrogen Peroxide. The reaction that results in the formation of most of the H_2O_2 is the radical-radical recombination involving $OH^\cdot$:

The G value for the formation of H_2O_2 is 0.7 and therefore the formation of significant concentrations of this relatively stable oxidant are likely.

A second source of H_2O_2 in oxygenated aqueous solutions are the reactions of e^-_{aq} and $H^\cdot$ with O_2 . Both of these reactions result in the formation of reduced oxygen, the superoxide radical ion and/or the conjugate acid:

The products of equation 19 and 20 are in equilibrium, with a $pK_a = 4.8$. These products also lead to the formation of additional H_2O_2 :

The formation of H_2O_2 during the process and the possibility of the following reaction:

with a second order rate constant of $1.2 - 1.4 \times 10^{10} M^{-1} s^{-1}$, suggests that the addition of H_2O_2 to the influent stream may lead to an increase in the $OH^\cdot$ concentration. This would be significant if the solute of interest were removed primarily by reactions with the $OH^\cdot$.

Concentration of Reactive Species

One aspect of our research on high energy electron beam irradiation of toxic organic chemicals is to develop an understanding of the underlying chemistry. This understanding would be helpful in predicting, *a priori*, the success of the process for various applications. It is possible, using the estimate of absorbed dose described above and G values (equation 8), to determine the approximate concentration of the transient reactive species in irradiated aqueous solutions. The data for these calculations have been developed under laboratory conditions in pure water. Therefore, when natural waters are irradiated it is not yet possible to predict the exact concentration of the reactive species. However, we can estimate them, to a first approximation, using the following relationships:

$$1 \text{ erg} = 6.24 \times 10^5 \text{ MeV} = 6.24 \times 10^{11} \text{ eV} \quad [24]$$

it follows from Equation 1 that:

$$1 \text{ rad} = 6.24 \times 10^{13} \text{ eV g}^{-1} \quad [25]$$

and,

$$1 \text{ Mrad} = 6.24 \times 10^{19} \text{ eV g}^{-1} \quad [26]$$

$$= 6.24 \times 10^{22} \text{ eV L}^{-1} \text{ of H}_2\text{O} \quad [27]$$

For a chemical with a $G = 1$,

$$1 \text{ Mrad} = 6.24 \times 10^{22} \text{ eV L}^{-1} / 100 \text{ eV molecule}^{-1} \quad [28]$$

$$= 6.24 \times 10^{20} \text{ molecules L}^{-1} \text{ of H}_2\text{O} \quad [29]$$

dividing by Avogadro's number ($N_A = 6.02 \times 10^{23} \text{ molecules mole}^{-1}$), the result is,

$$1 \text{ Mrad} = 1.04 \times 10^{-3} \text{ mole L}^{-1} = 1.04 \text{ mM} \quad [30]$$

Thus, for a G value of 2.7, e.g., $\text{OH}\cdot$ from equation 9, and an absorbed dose of 1 Mrad, there are 2.81 mmol of $\text{OH}\cdot$ formed. Typical concentrations of these transient reactive species and H_2O_2 , at several doses, are summarized in Table 1.

Table 1. Estimated Concentration of Transient Reactive Species at Several Doses Using High Energy Electron Irradiation.

DOSE (krads)	e_{aq}^-	$H\cdot$	$OH\cdot$	H_2O_2
	mM			
100	0.27	0.06	0.28	0.07
500	1.4	0.3	1.4	0.4
1000	2.7	0.6	2.8	0.7

Influence of Transient Reactive Species on the Removal of
Toxic Organic Chemicals

It is possible to calculate the relative importance of the three transient reactive species on the removal of some organic compounds of interest in site remediation and hazardous waste treatment. These calculations are important in attempting to develop a quantitative understanding of removal efficiency in natural waters. It should be noted that the calculations use data that were obtained in laboratory experiments and are strictly applicable to only pure water. The extension of these calculations to natural waters involves additional steps to take into account the reaction of the transient reactive species with naturally occurring scavengers, e.g. oxygen, carbonate/bicarbonate, etc. A second problem that arises in using these data to predict removal efficiencies is that often times the reactions cited may be reversible and although the initial step should result in the removal of the solute, this is not always the case.

If we assume that the only processes responsible for the removal of an organic solute (R) from an irradiated solution are reactions with the three reactive species e_{aq}^- , $H\cdot$, and $OH\cdot$, then the overall removal of any solute can be described by the following kinetic expression:

$$-\frac{d[R]}{dt} = k_1[R][OH\cdot] + k_2[R][e_{aq}^-] + k_3[R][H\cdot] \quad [31]$$

where, k_1 , k_2 , k_3 , are the respective second order rate constants (Table III). The relative concentrations of each of the three reactive species in pure aqueous solution is given by the G value. Therefore, at any dose, the product of the second order rate constant of a given solute and the G value of the respective reactive species is a proportionality constant, k'_1 , k'_2 , k'_3 . The relative percentage removal of the solute by each of the reactive species can be determined from Equation 36, where the individual proportionality constant is divided by the sum of the three and converted to percent (by multiplying by 100), e.g. for $OH\cdot$:

$$\text{Relative Removal}_{[R]} = k'_1 / (k'_1 + k'_2 + k'_3) \times 100 \quad [32]$$

Summing these proportionality constants provides an estimation of the overall relative solute removal:

$$\text{Relative Solute Removal} = k'_i[R] \quad [33]$$

For example, Table 2 summarizes these calculations for two of the solutes of interest, benzene and phenol. The removal of benzene and phenol is almost entirely by $\text{OH}\cdot$. The relative solute removal of the two solutes (Table 2), in pure aqueous solution, k'_i , would be benzene > phenol. In waste streams, because of the presence of radical scavengers competing for the reactive species, this may not hold. However, once these calculations have been made, experiments can be designed using water of varying quality to test the hypothesis.

Table 2. Examples of Proportionality Constants of Selected Toxic Organic Chemicals with Reactive Species Formed During Irradiation.

	$\text{OH}\cdot$		$e^-_{(aq)}$		$\text{H}\cdot$		
	k'_1	% ^a	k'_2	% ^a	k'_3	% ^a	
	($\times 10^9$)		($\times 10^9$)		($\times 10^9$)		
Benzene	21.1	97.5	0.02	0.1	0.55	2.4	21.7
Phenol	17.8	93.7	0.05	0.003	1.19	6.3	19.0

^aPercent that each reactive species is responsible for solute removal.

^bAssuming a second order rate constant the same as TCE.

Irradiation Dose Constants

One quantitative method for comparing solute removal from irradiated solutions that we have developed is in the form of a dose constant, that is, the concentration of organic solute removed per unit dose (15). The assumption is, that the removal of organic solutes is first order in both the total reactive radical species ($\text{OH}\cdot$, e^-_{aq} , $\text{H}\cdot$) and organic solute.

The concentration of the reactive radicals formed in the irradiated solutions was calculated in Equation 34. Based on these calculations, the total reactive radical species concentration formed in all experiments ranged from 0.61 - 6.1 mM for $\text{OH}\cdot$, at doses of 100 to 1,000 krad. Under these conditions the loss of the solutes (at solute concentrations in the μM range) is pseudo-first-order, with respect to absorbed dose, and can be described by the following:

$$-\frac{d[R]}{dD} = k[R][\Sigma(\Theta)] = k_o [R] \quad [35]$$

Where, $[\Sigma(\Theta)]$, is the sum of the concentration of the reactive species, at dose D, whose concentration remains essentially constant, and k_o is the observed pseudo-first-order dose constant. (k_o can be obtained from the slope of the plot of $\ln [R]$ against dose (D).) Since solute removal from aqueous solutions exhibits pseudo-first-order behavior, the dose required for [R] to reach 99 % removal, can then be determined by the following:

$$D_{0.99} = (\ln 100)/(k_o) \quad [36]$$

Radical Scavenger Effects

An important consideration in extending laboratory data to natural waters is the effect of radical scavengers on the removal of the solute of interest. In hazardous site remediation these are generally the natural constituents of the water, while for industrial treatment they may be other organic chemicals not targeted for regulation. A compilation of the bimolecular rate constants for the reactive transient species and potential scavengers are shown in Table 3.

Oxygen. Both e_{aq}^- and $H\cdot$ rapidly reduce O_2 to form $O_2^{\cdot-}$ ($pK_a = 4.8$) (13). At a dose of 100 krad a dissolved oxygen concentration of 3.7 mg L^{-1} (0.12 mM) concentration would remove approximately 35% of the two reactive species. However, at 800 krad only 5% would be removed.

Bicarbonate/Carbonate Ion. A common $OH\cdot$ scavenger in natural waters is alkalinity. Alkalinity, the measure of the total carbonate concentration is further complicated by the equilibrium that exist in natural waters.

Based on the pH and equilibrium calculations the carbonate/bicarbonate ion distribution is quite different in the waters used for study at the EBRF. For example, the secondary wastewater has a pH = 7.0 whereas the potable water is approximately 9.0.

Table 3. Rate Constants ($M^{-1} s^{-1}$) of Chemical Species Commonly Found in Natural Waters and Transient Reactive Species Formed in Irradiated Aqueous Solution (13).

Compound	e_{aq}^-	$H^\bullet$	$HO^\bullet$
Bicarbonate ion	1.0×10^6	4.0×10^4	8.5×10^6
Bromide ion	NF	2.8×10^7	$1.1 \times 10^{10**}$
Carbonate ion	3.5×10^5	NF	3.9×10^8
Nitrate ion	9.7×10^9	1.4×10^6	NF
Oxygen	1.9×10^{10}	2.1×10^{10}	NF
Methanol	1.0×10^4	2.6×10^6	9.7×10^8

* many experiments conducted at low pH

** determined at pH = 1 and may be slower at near neutral pH

NF = not found

For example, the alkalinity of the secondary wastewater, pH = 6.78, and the potable water, pH = 8.64, in one set of experiments was 1900 and 360 μM , respectively. Although the alkalinity of the secondary wastewater was 5-fold higher than the potable water, the $OH^\bullet$ scavenging is approximately 2.5 times higher in the potable water based on bicarbonate/carbonate equilibria. This relationship was determined by summing the product of the concentration of the carbonate and bicarbonate ions with $OH^\bullet$ reaction rate constants in each water.

The reaction of the carbonate radical ion, $CO_3^{\bullet-}$, is not known for many solutes and therefore this process is considered as a loss of reactive species with no removal of solute.

Nitrate Ion. When comparing the removal of solutes in potable water and secondary wastewater, the presence of higher concentrations of nitrate ion (NO_3^-) in the secondary wastewater may effected solute removal efficiency by acting as an e_{aq}^- scavenger. By efficiently scavenging e_{aq}^- the effective concentration of the $OH^\bullet$ might be increased (minimizing recombination of the e_{aq}^- and $OH^\bullet$, thereby increasing the effective $OH^\bullet$ concentration) and removal enhanced. However, the NO_2^- ion is known to react with the $OH^\bullet$ and the resulting radical could lead to addition of $-NO_2$ to organic solutes.

Dissolved Organic Carbon. Another common component in natural waters is the poorly characterized fraction referred to as dissolved organic carbon, DOC. The difference in DOC concentration in secondary wastewater (6-fold higher than the potable water we used for our studies) may have also reduced removal efficiency by acting as an $OH^\bullet$ radical scavenger. There is no data on the reactions of either e_{aq}^- or $H^\bullet$ with DOC and only indirect evidence of the reaction with $OH^\bullet$.

Methods and Materials

Phenol, Substituted Phenols and Nitrobenzene by HPLC

This section describes a rapid liquid chromatographic method that has been developed for the quantitative determination of phenol and nitrophenols in water, groundwater and wastewater. The technique is based upon direct separation and subsequent quantification using UV-visible detection. This technique has been used successfully in characterizing and quantifying phenol and nitrophenols formed as a result of irradiation of organic compounds in different solutions and has been shown to be sensitive, selective, fast and easy-to-use.

High Performance Liquid Chromatography (HPLC). A Hewlett-Packard 1090 high performance liquid chromatograph (HPLC) with a 1040M diode-array UV/vis detection system was used for determinations of phenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and nitrobenzene. The column is a Hypersil 5 micron reverse phase C₁₈ column (2.1 mm x 100 mm i.d.). An isocratic elution program was used throughout: 90/10 (v/v) 1% acetic acid (pH = 2.8) and acetonitrile. The eluent flow rate was maintained at 0.5 mL min⁻¹ and the temperature of the column was controlled at 50° C. A wavelength of 278 nm was used for detection and the injection volume was 50 µL.

UV-Vis Detection and Library Files. Detection was performed by a HP 1040M diode-array detection system, and the wavelength for the detection was 278 nm for phenol and nitrophenols. In addition, the 1040M diode-array detector system records the absorbance at all wavelengths from 190 nm to 600 nm for each chromatographic peak component, the UV-Vis spectra of the standards can be stored in the library. Analysis of unknowns, phenol and nitrophenols, were compared with the stored library files, making an on-line confirmation and characterization of phenols possible. Therefore, the identification and characterization of phenols are not only based on their retention times, but also on the comparison of the specific chemical natures and molecular structures of phenolic compounds - a function of UV/vis spectrum with standards.

Detection Limit. The method detection limit for the five phenols was below 1 mg L⁻¹ for all phenols, without pre-concentrations procedures. The detection limits are reported on the basis of a signal to noise ratio 3:1. The method detection limits can be lowered by 10 to 100 times using solid-liquid phase extraction (C-18 SPE cartridge).

Calibration of HPLC. Standard phenols are prepared by dissolving the compounds (without further purification) into distilled water and preparing various solution concentrations by dilution. Aqueous phase injection to the HPLC system, in triplicate, results in calibration curves using chromatographic area vs concentrations. The calibration curves were linear (regression coefficient r^2 is greater than 0.999) over a concentration range from 1 mg L⁻¹ to 50 mg L⁻¹. The calibration curves were checked at least once a week or more frequently by using midpoint calibration standards (independently prepared). The response must be within one standard deviation of the expected mean for the system to be considered satisfactory.

Quality Control. All electronic equipment is allowed to warm up for 30 minutes before initial analyses. During this period, at least 15 void volumes of mobile phase are passed through the column or until the baseline is stabilized at the UV detector's greatest sensitivity.

Prior to unknown sample analyses, a method blank (samples with no phenols) was run. Four separate concentration levels should be tested, including one level at 1 mg L⁻¹, one at 50 mg L⁻¹ and two other concentration in the range. For each concentration level, seven replicate determinations were made, and the period for precision test was approximately two hours. The standard deviations were within 1%. Known concentrations of phenols were added (matrix spikes) into samples to check the accuracy for each analytical batch. Triplicate matrix spikes were required. The percent recovery for all six phenols was higher than 90% over the entire concentration ranges tested. All samples were run at least in triplicate and the mean concentration reported.

Automated Headspace Gas Chromatography Technique for the Analysis of Volatile Pollutants

Headspace sampling has been widely used for the analysis of volatiles in virtually any matrix and has often been applied to environmental samples such as air, water, soil and sludge. Instruments for automatic headspace analysis require that the sample be placed in a glass vial (typical volume-22 mL) which is sealed with a septum and aluminum crimp cap. After achieving equilibrium at an elevated temperature, a reproducible aliquot of the headspace is delivered to the gas chromatograph.

Though often confusing, purge and trap has sometimes been referred to as "dynamic headspace" while the equilibration method is called static headspace. To avoid confusion the headspace term is used herein.

A Hewlett-Packard 5890 Gas Chromatograph equipped with a HP 19395A Headspace sampler, HNU PI 52-02A photoionization detector (PID) and OI 4420 electrolytic conductivity Detector (ELCD). Detector signals were communicated with E-LabTM chromatographic control and data acquisition system (OMS Tech).

For series operation of the two detectors, effluent from the PID was transferred to the ELCD using a 23 cm x 0.53 mm i.d. section of uncoated deactivated fused silica.

General Conditions for Chromatographic Analysis.

Headspace Conditions:

thermostating temp. 60°C (except where noted)
valve and loop temp. 65°C (or 5°C above thermostating temp)

Sample loop volume 1.0mL

Typical injection sequence

probe down 0:01 min : sec
start pressurization 0:03
stop pressurization 0:13
start venting 0:14
stop venting 0:19
start injecting 0:20
stop injecting 0:30
probe up 0:31

auxiliary pressure 1.0 - 1.2 bar

carrier flow rate He @ 8 mL/min

oven 30°C (5 min), to 65°C (3°/min), then to 150°C (6°/min) and held for 2 min

make up gas HE @ 22 mL/min

ELCD Conditions:

mode Halogen
hydrogen flow rate 100mL/min
2-propanol flow rate 30 μ L/min
detector base temp 250°C
reactor temp 850°C

PID conditions:

lamp 10.2 ev
detector base temp 250°C
lamp intensity 50% of scale
column DB-5; 30m x 0.53 mm i.d.
film thickness 3.0 μ m

all capillary analyses were run using DB-5 connected to the sampler's transfer line on the top of the GC oven.

Optimization of Headspace Sensitivity Instrumental Considerations. The HP 19395A Headspace Sampler uses a valve and loop configuration system. Normally, the septum-sealed vial is first pressurized with carrier gas by means of a sampling needle which pierces the septum

to initiate the injection sequence. The pressurized headspace gas then vents through the sampling needle and sample loop to the atmosphere. Once filled, the loop is placed in series with the normal carrier gas flow and its contents are driven through the heated transfer line to the GC injection port.

For these analyses a 1.0 mL sample loop was installed. To achieve high sensitivity, the vial should be pressurized only slightly above that pressure which develops internally when the aqueous sample is heated. A value of 1.2 bar was chosen for many of these analyses. However, when the vial pressurization step is skipped altogether, the headspace is not diluted with additional helium and maximum sensitivity is often achieved. With 10 mL aqueous samples, the internal pressure developed upon heating is sufficient to purge the sample loop, allowing the pressurization step to be omitted. When using 15 mL samples thermostated at 60°C and 1.0 mL samples, it is necessary to pressurize the vial between 1.1 and 1.2 bar in order to purge the loop completely. When using 15-mL samples thermostated at 60°C and a 1.0 mL samples, it is necessary to pressurize the vial between 1.1 and 1.2 bar in order to purge the loop completely.

Bath Temperature. The temperature at which the sample is equilibrated strongly affects the concentration of analytes which partitions into the headspace gas. In general, as the bath temperature increases, the amount of analyte delivered to the gas chromatograph, and thus the sensitivity of the method also increases. Best results are obtained if the temperature of the bath is maintained at a level just high enough to safely provide the desired analytical sensitivity. All subsequent samples were thermostated at 60°C for a minimum of three GC analysis times.

Constant Heating Time. This method used constant heating time (CHT) attachment for the Hewlett Packard 19395A headspace sampler, a device which allowed every vial to be heated for the same period of time (Three GC analysis times in this case).

Sample Preparation Consideration. The addition of an inorganic salt to aqueous solutions is known to increase the sensitivity of headspace analyses by decreasing the solubility of organic molecules (the salting out effect). The effect is more dramatic for polar compounds particularly those which hydrogen bond.

Sample Loop Size. The sampler has a 1.0 mL sample loop that was used exclusively throughout this project.

Method detection limits (MDL) for benzene using the PID by headspace technique was 0.03 $\mu\text{g L}^{-1}$.

Preliminary Results

Table 4 summarizes the experimental design for the preliminary ^{60}Co irradiation of the four solutes of interest. Based on the approved research plan #SRL-A1-Ver 1.0-920615. Tables 5 - 10 summarize the results obtained on the decomposition of benzene, benzene reaction by-products, phenol, phenol reaction by-products, 4-nitrophenol and nitrobenzene, respectively. All of the data were obtained using the approved project QA/QC plan. To determine the magnitude of the effects of various constituents on the removal efficiency of the solutes a full factorial design was employed. Figures 1 - 4 summarize the removal data in Tables 5, 7, 9, and 10, respectively.

Table 4. Savannah River Project ^{60}Co Experimental Key.

Experiment	Additives*
1	No additives
2	200 mg L ⁻¹ TOC as Alconox TM
3	900 mg L ⁻¹ NO ₃ ⁻ ion
4	390 mg L ⁻¹ SO ₄ ²⁻ ion
5	1740 mg L ⁻¹ PO ₄ ³⁻ ion
6	10 mg L ⁻¹ Fe ²⁺ ion
7	200 mg L ⁻¹ TOC as Alconox TM 900 mg L ⁻¹ NO ₃ ⁻ ion
8	200 mg L ⁻¹ TOC as Alconox TM 390 mg L ⁻¹ SO ₄ ²⁻ ion
9	200 mg L ⁻¹ TOC as Alconox TM 1740 mg L ⁻¹ PO ₄ ³⁻ ion
10	200 mg L ⁻¹ TOC as Alconox TM 10 mg L ⁻¹ Fe ²⁺ ion
11	900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion
12	900 mg L ⁻¹ NO ₃ ⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion
13	900 mg L ⁻¹ NO ₃ ⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion
14	390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion
15	390 mg L ⁻¹ SO ₄ ²⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion
16	1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion

Table 4 (cont.). Savannah River Project ⁶⁰Co Experimental Key.

Experiment	Additives*
17	390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion
18	900 mg L ⁻¹ NO ₃ ⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion
19	900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 10 mg L ⁻¹ Fe ²⁺ ion
20	900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion
21	200 mg L ⁻¹ TOC as Alconox TM 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺
22	200 mg L ⁻¹ TOC as Alconox TM 390 mg L ⁻¹ SO ₄ ²⁻ ion 10 mg L ⁻¹ Fe ²⁺
23	200 mg L ⁻¹ TOC as Alconox TM 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion
24	200 mg L ⁻¹ TOC as Alconox TM 900 mg L ⁻¹ NO ₃ ⁻ ion 10 mg L ⁻¹ Fe ²⁺
25	200 mg L ⁻¹ TOC as Alconox TM 900 mg L ⁻¹ NO ₃ ⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion

Table 4 (cont.). Savannah River Project ⁶⁰Co Experimental Key.

Experiment	Additives*
26	200 mg L ⁻¹ TOC as Alconox™ 900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion
27	200 mg L ⁻¹ TOC as Alconox™ 900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion
28	200 mg L ⁻¹ TOC as Alconox™ 900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 10 mg L ⁻¹ Fe ²⁺
29	200 mg L ⁻¹ TOC as Alconox™ 900 mg L ⁻¹ NO ₃ ⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺
30	200 mg L ⁻¹ TOC as Alconox™ 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺
31	900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺
32	200 mg L ⁻¹ TOC as Alconox™ 900 mg L ⁻¹ NO ₃ ⁻ ion 390 mg L ⁻¹ SO ₄ ²⁻ ion 1740 mg L ⁻¹ PO ₄ ³⁻ ion 10 mg L ⁻¹ Fe ²⁺
*All experiments were conducted with a nominal concentration of compound N of 100 mg L ⁻¹ . In addition, all experimental solutions were adjusted to pH 3 with 12 N HCl prior to irradiation	

Table 5. Removal of benzene (nominally 100 mg L⁻¹) from aqueous solution using ⁶⁰Co-gamma radiation.

EXP	0 krad (mg L ⁻¹)	775 krad (mg L ⁻¹)	Percent Removed
1	112.40 ± 1.56	1.28 ± 0.08	98.86
	118.05 ± 0.78	1.37 ± 0.01	98.83
2	102.17 ± 4.37	16.21 ± 0.09	84.14
3	113.40 ± 0.28	13.99 ± 0.38	86.66
	113.95 ± 0.92	14.40 ± 0.23	87.36
4	108.35 ± 0.50	0.013 ± 0.001	99.99
	109.60 ± 0.85	0.014 ± 0.001	99.99
5	104.15 ± 0.64	0.013 ± 0.001	99.99
	115.75 ± 0.92	0.012 ± 0.001	99.99
6	112.05 ± 2.05	8.42 ± 0.11	92.48
	115.50 ± 1.70	8.29 ± 0.20	92.82
7	114.05 ± 2.19	42.56 ± 0.06	62.69
8	115.92 ± 6.22	19.20 ± 0.01	83.44
9	101.82 ± 3.22	18.55 ± 0.01	81.87
10	104.00 ± 2.69	28.40 ± 0.01	72.69
11	117.35 ± 1.06	13.68 ± 0.06	88.34
	114.75 ± 0.07	14.21 ± 0.04	87.62
12	116.60 ± 0.57	15.92 ± 0.18	86.35
	115.10 ± 1.13	16.09 ± 0.16	86.03
13	119.95 ± 0.35	9.79 ± 0.13	91.84
	115.80 ± 0.00	10.06 ± 0.09	91.32
14	107.95 ± 7.99	0.91 ± 0.07	99.16
	108.70 ± 1.13	0.88 ± 0.06	99.20
15	109.80 ± 4.81	6.69 ± 0.12	93.91
	110.85 ± 0.92	6.61 ± 0.13	94.03
16	111.60 ± 0.57	0.77 ± 0.02	99.31
	110.20 ± 0.00	0.81 ± 0.01	99.27

Table 5 (cont.). Removal of benzene (nominally 100 mg L⁻¹) from aqueous solution using ⁶⁰Co-gamma radiation, continued.

EXP	0 krad (mg L ⁻¹)	775 krad (mg L ⁻¹)	Percent Removed
17	113.80 ± 1.27	0.79 ± 0.06	99.31
	111.35 ± 1.20	0.78 ± 0.02	99.30
18	96.37 ± 0.74	17.23 ± 0.23	82.13
	93.79 ± 1.17	17.14 ± 0.08	81.73
19	98.61 ± 1.29	11.67 ± 0.38	88.17
	96.94 ± 0.18	11.48 ± 0.01	88.16
20	113.95 ± 3.89	21.08 ± 0.32	81.51
	107.20 ± 0.57	21.39 ± 0.28	80.05
21	115.75 ± 1.20	22.62 ± 0.08	80.46
22	114.30 ± 0.42	30.35 ± 0.18	73.45
23	97.56 ± 4.33	13.14 ± 0.03	86.53
24	110.87 ± 4.96	44.86 ± 0.84	59.54
25	110.19 ± 4.34	50.58 ± 0.94	54.10
26	106.76 ± 8.68	47.18 ± 0.69	55.81
27	100.20 ± 3.28	38.39 ± 0.37	61.69
28	92.68 ± 1.19	41.94 ± 5.08	54.75
29	103.89 ± 0.01	27.58 ± 1.38	73.46
30	91.30 ± 0.93	12.01 ± 0.04	86.85
31	108.60 ± 2.26	19.26 ± 0.09	82.27
	109.20 ± 1.70	19.25 ± 0.15	82.38
32	104.68 ± 1.62	36.54 ± 0.57	65.10

Table 6. Reaction Byproducts from the ^{60}Co Irradiation of 100 mg L Benzene (pH 3, 775 krad).

EXP	PHENOL (mg L ⁻¹)	PYROGALLOL (mg L ⁻¹)	HYDROQUINONE (mg L ⁻¹)	RESORCINOL (mg L ⁻¹)	CATECHOL (mg L ⁻¹)	2-NITROPHENOL (mg L ⁻¹)	4-NITROPHENOL (mg L ⁻¹)	NITROBENZENE (mg L ⁻¹)
1	0.92 ± 0.00	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
2	26.48 ± 0.02	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
3	11.80 ± 0.03	BMDL	BMDL	BMDL	BMDL	1.43 ± 0.01	0.15 ± 0.00	3.41 ± 0.01
4	0.29 ± 0.00	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
5	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
6	13.71 ± 0.10	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
7	1.89 ± 0.02	BMDL	BMDL	BMDL	BMDL	2.78 ± 0.01	2.18 ± 0.06	2.99 ± 0.01
8	26.70 ± 0.05	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
9	20.87 ± 0.06	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
10	24.96 ± 0.08	BMDL	1.34 ± 0.09	BMDL	BMDL	BMDL	BMDL	BMDL
11	13.11 ± 0.31	BMDL	BMDL	BMDL	BMDL	1.38 ± 0.03	0.15 ± 0.00	3.20 ± 0.05
12	8.35 ± 0.02	BMDL	BMDL	BMDL	BMDL	1.11 ± 0.01	0.11 ± 0.00	3.34 ± 0.00
13	8.90 ± 1.51	BMDL	BMDL	BMDL	BMDL	0.46 ± 0.22	0.18 ± 0.02	1.78 ± 0.07
14	1.26 ± 0.01	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
15	12.84 ± 0.05	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
16	1.63 ± 0.01	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL

BMDL = below method detection limit

Table 6 (cont.). Reaction Byproducts from the Co Irradiation of 100 mg L^{-1} Benzene ($\text{pH } 3$, 775 krad), continued.

EXP	PHENOL (mg L^{-1})	PYROGALLOL (mg L^{-1})	HYDROQUINONE (mg L^{-1})	RESORCINOL (mg L^{-1})	CATECHOL (mg L^{-1})	2-NITROPHENOL (mg L^{-1})	4-NITROPHENOL (mg L^{-1})	NITROBENZENE (mg L^{-1})
					BMDL	BMDL	BMDL	BMDL
17	1.45 ± 0.02	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
18	14.19 ± 0.07	9.16 ± 0.20	BMDL	2.01 ± 0.01	3.53 ± 0.03	0.69 ± 0.00	0.14 ± 0.00	1.83 ± 0.00
19	14.90 ± 0.02	43.65 ± 0.91	0.22 ± 0.00	2.19 ± 0.00	0.62 ± 0.01	BMDL	0.32 ± 0.00	1.97 ± 0.00
20	12.89 ± 0.08	12.30 ± 0.20	0.75 ± 0.07	1.25 ± 0.20	3.76 ± 0.15	0.75 ± 0.01	0.15 ± 0.00	1.79 ± 0.02
21	20.61 ± 0.13	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
22	24.77 ± 0.03	BMDL	0.80 ± 0.01	BMDL	BMDL	BMDL	BMDL	BMDL
23	18.86 ± 0.07	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
24	23.47 ± 0.06	BMDL	BMDL	BMDL	BMDL	2.65 ± 0.02	2.09 ± 0.02	2.04 ± 0.03
25	18.48 ± 0.23	BMDL	BMDL	BMDL	BMDL	4.37 ± 0.01	3.32 ± 0.01	10.66 ± 0.06
26	3.69 ± 0.07	BMDL	BMDL	BMDL	BMDL	2.37 ± 0.00	1.85 ± 0.00	2.70 ± 0.01
27	15.00 ± 0.04	BMDL	BMDL	BMDL	BMDL	5.86 ± 0.03	4.44 ± 0.01	11.22 ± 0.10
28	2.08 ± 0.01	BMDL	BMDL	BMDL	BMDL	2.33 ± 0.01	1.80 ± 0.00	2.53 ± 0.01
29	12.70 ± 0.06	BMDL	BMDL	BMDL	BMDL	5.58 ± 0.02	4.21 ± 0.02	10.99 ± 0.01
30	16.13 ± 0.05	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
31	11.61 ± 0.07	12.29 ± 0.47	BMDL	1.96 ± 0.14	3.50 ± 0.09	0.71 ± 0.00	0.16 ± 0.00	2.04 ± 0.02
32	15.36 ± 0.00	BMDL	BMDL	BMDL	BMDL	4.93 ± 0.06	3.75 ± 0.01	11.14 ± 0.01

BMDL = below method detection limit

Table 7. Removal of phenol (nominally 100 mg L⁻¹) from aqueous solution using ⁶⁰Co-gamma radiation.

EXP	0 krad (mg L ⁻¹)	775 krad (mg L ⁻¹)	Percent Removed
1	95.86 ± 0.59	55.17 ± 0.11	42.45
2	95.76 ± 0.11	72.19 ± 1.29	24.62
3	94.16 ± 0.03	16.76 ± 0.00	82.20
4	95.53 ± 0.86	55.54 ± 0.11	41.86
5	80.21 ± 0.47	53.29 ± 0.04	33.57
6	89.41 ± 0.22	53.36 ± 0.05	40.33
7	96.72 ± 0.15	9.619 ± 0.007	90.06
8	95.42 ± 0.98	72.39 ± 0.00	24.14
9	95.85 ± 0.04	67.49 ± 0.34	29.59
10	96.34 ± 1.39	76.44 ± 0.05	20.65
11	97.15 ± 0.12	11.60 ± 0.07	88.06
12	97.75 ± 0.38	10.79 ± 0.27	88.97
13	96.23 ± 0.25	6.93 ± 0.06	92.80
14	96.86 ± 0.04	46.79 ± 0.24	51.69
15	97.00 ± 0.57	50.44 ± 0.01	48.00
16	97.05 ± 0.96	50.89 ± 0.04	47.56
17	95.92 ± 0.01	51.87 ± 0.07	45.93
18	95.98 ± 0.36	13.79 ± 0.04	85.63
19	96.98 ± 0.09	11.15 ± 0.35	88.50
20	98.18 ± 1.16	16.05 ± 0.30	83.65
21	88.07 ± 0.10	70.80 ± 0.59	19.62
22	97.80 ± 0.06	78.27 ± 0.41	19.98
23	98.39 ± 0.02	65.95 ± 0.13	32.98
24	98.92 ± 0.52	22.13 ± 0.01	77.63
25	100.24 ± 0.28	50.58 ± 0.01	49.55
26	100.58 ± 0.08	22.70 ± 0.07	77.43
27	99.81 ± 0.40	50.54 ± 0.04	49.36
28	98.86 ± 0.13	24.20 ± 0.01	75.52
29	96.40 ± 0.09	52.77 ± 0.08	45.26
30	96.83 ± 0.19	62.94 ± 0.01	35.00
31	96.84 ± 0.08	20.52 ± 0.20	78.81
32	95.93 ± 0.02	52.97 ± 0.02	44.78

Table 8. Reaction Byproducts from the ^{60}Co Irradiation of 100 mg L⁻¹ Phenol (pH 3, 775 krad).

EXP	PYROGALLOL (mg L ⁻¹)	HYDROQUINONE (mg L ⁻¹)	RESORCINOL (mg L ⁻¹)	CATECHOL (mg L ⁻¹)	2-NITROPHENOL (mg L ⁻¹)	4-NITROPHENOL (mg L ⁻¹)
1	BMDL	2.05 ± 0.01	0.88 ± 0.08	18.40 ± 0.12	BMDL	BMDL
2	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
3	BMDL	BMDL	2.64 ± 0.14	0.40 ± 0.01	0.57 ± 0.00	0.06 ± 0.00
4	BMDL	1.58 ± 0.01	0.86 ± 0.01	15.66 ± 0.05	BMDL	BMDL
5	BMDL	1.99 ± 0.07	1.08 ± 0.02	21.22 ± 0.30	BMDL	BMDL
6	BMDL	2.65 ± 0.13	1.00 ± 0.12	13.76 ± 0.39	BMDL	BMDL
7	BMDL	BMDL	BMDL	BMDL	2.30 ± 0.01	0.19 ± 0.00
8	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
9	BMDL	0.41 ± 0.01	1.06 ± 0.01	1.45 ± 0.03	BMDL	BMDL
10	BMDL	BMDL	0.42 ± 0.01	BMDL	BMDL	BMDL
11	BMDL	BMDL	2.26 ± 0.30	0.55 ± 0.08	0.41 ± 0.00	0.05 ± 0.00
12	BMDL	BMDL	2.15 ± 0.03	0.32 ± 0.00	0.44 ± 0.01	0.05 ± 0.00
13	BMDL	BMDL	1.57 ± 0.01	BMDL	BMDL	0.05 ± 0.01
14	2.03 ± 17	4.34 ± 0.05	0.44 ± 0.04	26.13 ± 0.06	BMDL	BMDL
15	BMDL	2.95 ± 0.01	0.86 ± 0.11	15.99 ± 0.39	BMDL	BMDL
16	1.87 ± 0.00	3.55 ± 0.13	0.33 ± 0.12	22.86 ± 0.64	BMDL	BMDL

BMDL = below method detection limit

Table 8 (cont.). Reaction Byproducts from the ⁶⁰Co Irradiation of 100 mg L Phenol (pH 3, 775 krad), continued.

EXP	PYROGALLOL (mg L ⁻¹)	HYDROQUINONE (mg L ⁻¹)	RESORCINOL (mg L ⁻¹)	CATECHOL (mg L ⁻¹)	2-NITROPHENOL (mg L ⁻¹)	4-NITROPHENOL (mg L ⁻¹)
17	1.34 ± 0.01	3.57 ± 0.04	0.44 ± 0.02	22.67 ± 0.08	BMDL	BMDL
18	BMDL	BMDL	2.27 ± 0.07	BMDL	0.27 ± 0.00	0.03 ± 0.00
19	BMDL	BMDL	2.02 ± 0.00	BMDL	BMDL	0.05 ± 0.00
20	BMDL	BMDL	2.27 ± 0.02	BMDL	0.45 ± 0.01	0.05 ± 0.00
21	BMDL	1.07 ± 0.04	BMDL	5.40 ± 0.04	BMDL	BMDL
22	BMDL	BMDL	0.33 ± 0.03	0.15 ± 0.00	BMDL	BMDL
23	3.13 ± 0.04	0.84 ± 0.04	0.99 ± 0.00	3.14 ± 0.15	BMDL	BMDL
24	BMDL	BMDL	0.30 ± 0.01	BMDL	1.98 ± 0.00	1.53 ± 0.00
25	1.95 ± 0.19	0.73 ± 0.00	BMDL	6.35 ± 0.07	BMDL	BMDL
26	1.02 ± 0.03	BMDL	BMDL	BMDL	2.00 ± 0.03	1.55 ± 0.01
27	1.71 ± 0.01	0.89 ± 0.04	BMDL	5.58 ± 0.04	BMDL	BMDL
28	BMDL	BMDL	0.30 ± 0.00	BMDL	1.92 ± 0.01	1.48 ± 0.00
29	1.99 ± 0.03	0.24 ± 0.02	BMDL	3.64 ± 0.01	BMDL	BMDL
30	4.06 ± 0.05	1.20 ± 0.00	0.51 ± 0.01	8.94 ± 0.02	BMDL	BMDL
31	BMDL	0.56 ± 0.00	BMDL	BMDL	BMDL	0.78 ± 0.00
32	2.16 ± 0.14	0.20 ± 0.00	BMDL	2.93 ± 0.00	BMDL	BMDL

BMDL = below method detection limit

Table 9. Removal of 4-nitrophenol (nominally 100 mg L⁻¹) from aqueous solution using ⁶⁰Co-gamma radiation.

EXP	0 krad (mg L ⁻¹)	775 krad (mg L ⁻¹)	Percent Removed
1	94.89 ± 0.06	2.01 ± 0.01	97.89
2	96.36 ± 0.03	10.58 ± 0.02	89.02
3	95.15 ± 0.15	3.20 ± 0.03	96.63
4	95.59 ± 0.04	2.06 ± 0.01	97.85
5	94.68 ± 0.09	2.10 ± 0.00	97.79
6	94.91 ± 0.01	1.53 ± 0.00	98.39
7	95.55 ± 0.13	30.41 ± 0.03	68.18
8	96.95 ± 0.04	11.47 ± 0.00	88.17
9	95.64 ± 0.05	8.10 ± 0.02	91.53
10	93.58 ± 0.01	6.05 ± 0.01	93.54
11	94.94 ± 0.23	3.30 ± 0.01	96.53
12	93.81 ± 0.15	6.66 ± 0.00	92.91
13	94.63 ± 0.23	2.38 ± 0.00	97.48
14	95.14 ± 0.10	1.62 ± 0.00	98.30
15	95.22 ± 0.01	1.18 ± 0.01	98.76
16	92.82 ± 0.24	1.69 ± 0.03	98.18
17	94.10 ± 0.11	1.59 ± 0.02	98.31
18	93.04 ± 0.06	6.01 ± 0.01	93.54
19	95.79 ± 0.09	3.32 ± 0.01	96.54
20	96.56 ± 0.21	7.82 ± 0.01	91.91
21	93.45 ± 0.01	6.82 ± 0.05	92.70
22	93.90 ± 0.14	8.34 ± 0.01	91.11
23	96.12 ± 0.07	8.83 ± 0.01	90.82
24	92.64 ± 0.11	25.48 ± 0.06	72.49
25	96.71 ± 0.20	28.01 ± 0.02	71.04
26	94.56 ± 0.03	27.51 ± 0.00	71.03
27	94.99 ± 0.15	27.27 ± 0.01	71.29
28	94.01 ± 0.17	24.67 ± 0.04	73.76
29	91.64 ± 0.02	24.98 ± 0.01	72.74
30	92.28 ± 0.06	5.30 ± 0.00	94.26
31	95.23 ± 0.10	6.96 ± 0.02	92.70
32	90.38 ± 0.10	25.51 ± 0.01	71.78

Table 10. Removal of nitrobenzene (nominally 100 mg L⁻¹) from aqueous solution using ⁶⁰Co-gamma radiation.

EXP	0 krad (mg L ⁻¹)	775 krad (mg L ⁻¹)	Percent Removed
1	93.74 ± 0.01	22.27 ± 0.04	76.25
2	93.37 ± 0.16	27.31 ± 0.04	70.76
3	94.02 ± 0.15	5.66 ± 0.06	93.98
4	93.75 ± 0.02	21.42 ± 0.01	77.16
5	92.58 ± 0.00	24.99 ± 0.01	73.01
6	92.74 ± 0.19	18.77 ± 0.02	79.76
7	93.24 ± 0.23	44.65 ± 0.09	52.11
8	93.69 ± 0.10	27.14 ± 0.00	71.04
9	94.08 ± 0.00	28.89 ± 0.01	69.29
10	94.18 ± 0.00	28.95 ± 0.05	69.26
11	92.97 ± 0.01	7.13 ± 0.08	92.33
12	94.35 ± 0.05	11.67 ± 0.09	87.64
13	94.04 ± 0.11	8.47 ± 0.01	90.99
14	92.16 ± 0.00	26.52 ± 0.03	71.23
15	93.24 ± 0.04	20.36 ± 0.00	78.17
16	91.10 ± 0.08	22.46 ± 0.01	75.35
17	90.08 ± 0.12	20.01 ± 0.02	77.79
18	89.15 ± 0.00	9.90 ± 0.11	88.90
19	87.75 ± 0.05	7.07 ± 0.01	91.94
20	86.53 ± 0.14	9.48 ± 0.00	89.04
21	87.05 ± 0.12	21.18 ± 0.01	75.67
22	89.33 ± 0.33	20.04 ± 0.05	77.57
23	88.02 ± 0.00	24.48 ± 0.01	72.19
24	82.96 ± 0.51	37.19 ± 0.18	55.18
25	91.34 ± 0.49	43.41 ± 0.02	52.48
26	92.17 ± 0.33	45.26 ± 0.13	50.90
27	91.43 ± 0.68	45.10 ± 0.09	50.68
28	88.94 ± 0.43	47.50 ± 0.19	46.59
29	91.07 ± 0.07	45.89 ± 0.12	49.62
30	93.27 ± 0.31	24.31 ± 0.25	73.93
31	84.65 ± 0.00	3.81 ± 0.01	95.49
32	90.78 ± 0.42	5.58 ± 0.05	93.85

Figure 1. Percent benzene remaining in cobalt 60 experiments

Figure 2. Percent phenol remaining in cobalt 60 experiments

Figure 3. Percent 4-nitrophenol remaining in cobalt 60 experiments

Figure 4. Percent nitrobenzene remaining in cobalt 60 experiments

Results of Full Scale (100 Gallons per minute) Study

Based on the data obtained during the preliminary studies conducted using ^{60}Co γ irradiation a "full scale" experiment was designed to determine the dose required to destroy benzene to the predetermined concentration level. The treatment objective was $5 \mu\text{g L}^{-1}$, the drinking water MCL (Maximum Contaminant Level).

To conduct the full scale experiment, 3000 gallons of the simulated lab waste had to be prepared. This was accomplished by using the chemicals and quantities listed in Table 11.

Table 11. Quantities of Chemicals Required for Full Scale Simulated Savannah River Low Activity Waste - Benzene Removal Study.		
Additive	Quantity added to 11,400 L (3,000 gal)	Target concentration
Benzene	1.6 liters	100 mg L ⁻¹ Benzene
NaNO ₃	14 kg	900 mg L ⁻¹ NO ₃ ⁻
Na ₂ SO ₄	6.5 kg	390 mg L ⁻¹ SO ₄ ²⁻
KH ₂ PO ₄	28.3 kg	1740 mg L ⁻¹ PO ₄ ³⁻
FeCl ₂ ·4H ₂ O	404 g	10 mg L ⁻¹ Fe ²⁺
Alconox TM soap	11.4 kg	200 mg L ⁻¹ TOC

To achieve the desired dose it was necessary to recirculate the same water several times. The experiment was designed for five recirculations at doses 300, 500 and 800 krad, with an initial and two additional zero doses. This design provided data for the removal of benzene at several initial concentrations. The actual design, i.e. dose and time of irradiation are presented in Figure 5.

Tables 12 and 13 summarize all of the data obtained for the removal of benzene and the formation of the reaction by-products during the recirculation study. Nitrobenzene was determined by two different analytical procedures, gas chromatography and high performance liquid chromatography and the results shown Tables 12 and 13.

Figures 6 - 15 graphically summarize the data in Tables 12 and 13. Figure 16 shows the total organic carbon data.

Figure 5. Dose/Time relationship for full-scale recirculation experiment

Table 12. Recirculation Experiment Benzene Removal and Nitrobenzene Formation and Destruction as Determined by GC.				
Dose (krad)	Benzene (mg L ⁻¹)		Nitrobenzene (mg L ⁻¹)	
	influent	effluent	influent	effluent
0 (R#1)	35.7 33.4	29.5 27.0	BMDL BMDL	BMDL BMDL
300 (R#1)	22.2 22.7	5.80 5.80	3.87 3.89	3.72 3.76
500 (R#1)	12.1 12.3	1.44 1.43	1.93 1.92	5.31 5.21
800 (R#1)	6.72 6.60	0.170 0.167	1.76 1.76	1.98 2.00
300 (R#2)	0.249 0.246	0.168 0.168	2.39 2.36	1.79 1.80
500 (R#2)	0.232 0.234	0.162 0.160	2.24 2.25	1.02 1.02
800 (R#2)	0.214 0.213	0.145 0.144	1.89 1.99	1.31 1.32
0 (R#3)	0.160 0.162	0.113 0.113	1.13 1.09	0.846 0.840
300 (R#3)	0.151 0.150	0.103 0.104	0.848 0.838	0.707 0.699
500 (R#3)	0.144 0.144	0.046 0.045	0.803 0.800	0.481 0.489
800 (R#3)	0.112 0.112	0.022 0.022	0.788 0.791	0.438 0.442
300 (R#4)	0.098 0.098	0.020 0.020	0.469 0.481	0.440 0.438
500 (R#4)	0.087 0.088	0.014 0.014	0.457 0.455	0.383 0.383
800 (R#4)	0.070 0.070	0.014 0.015	0.443 0.438	BMDL BMDL
0 (R#5)	0.055 0.051	0.010 0.010	0.381 0.379	BMDL BMDL
300 (R#5)	0.050 0.050	0.010 0.010	0.385 0.380	BMDL BMDL
500 (R#5)	0.047 0.050	0.009 0.009	0.376 0.362	BMDL BMDL
800 (R#5)	0.040 0.037	0.009 0.008	BMDL BMDL	BMDL BMDL

Table 13. Recirculation Experiment - Reaction By-products as Determined by HPLC.										
Dose (krad)	Phenol (mg L ⁻¹)		Nitrobenzene (mg L ⁻¹)		2-Nitrophenol (mg L ⁻¹)		4-Nitrophenol (mg L ⁻¹)		2,4-Dinitrophenol (mg L ⁻¹)	
	influent	effluent	influent	effluent	influent	effluent	influent	effluent	influent	effluent
0 (R#1)	BMDL BMDL	0.36 0.32	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
300 (R#1)	1.91 2.03	3.78 3.94	1.42 1.41	4.61 4.60	BMDL BMDL	1.38 1.37	0.31 0.32	1.15 1.17	0.39 0.37	0.06 0.06
500 (R#1)	2.37 2.25	1.91 1.86	2.14 2.16	3.38 3.38	0.74 0.74	1.57 1.57	0.60 0.59	1.33 1.33	0.73 0.76	0.15 0.15
800 (R#1)	1.86 1.96	0.18 0.18	2.30 2.32	1.90 1.89	0.98 0.93	1.13 1.13	0.82 0.84	0.95 0.96	0.09 0.09	0.18 0.19
300 (R#2)	1.26 1.27	0.58 0.54	2.52 2.53	2.15 2.15	1.17 1.18	0.94 1.07	1.01 0.99	0.88 0.88	0.15 0.15	0.18 0.18
500 (R#2)	0.60 1.09	BMDL BMDL	2.33 2.33	1.32 1.32	1.09 0.99	0.59 0.58	0.95 0.94	0.58 0.57	0.14 0.15	0.18 0.18
800 (R#2)	0.89 0.82	BMDL BMDL	1.95 1.94	0.75 0.73	0.86 0.84	0.31 0.30	0.80 0.80	0.31 0.31	0.16 0.15	0.15 0.15
0 (R#3)	BMDL BMDL	BMDL BMDL	0.99 1.00	0.98 0.99	0.41 0.43	0.43 0.42	0.41 0.42	0.41 0.41	0.14 0.15	0.15 0.14
300 (R#3)	BMDL BMDL	0.25 0.25	0.93 0.95	0.60 0.62	0.40 0.40	0.25 0.24	0.39 0.40	0.26 0.26	0.14 0.13	0.14 0.14
500 (R#3)	BMDL BMDL	0.26 0.26	0.81 0.81	0.34 0.38	0.33 0.34	0.12 0.13	0.35 0.34	0.13 0.13	0.13 0.14	0.11 0.13
800 (R#3)	BMDL BMDL	0.29 0.38	0.68 0.67	0.19 0.20	0.31 0.27	0.06 0.06	0.29 0.28	0.06 0.06	0.15 0.13	0.10 0.10
300 (R#4)	0.42 0.49	0.33 0.36	0.27 0.26	0.14 0.18	0.10 0.09	0.07 0.05	0.10 0.10	BMDL BMDL	0.11 0.10	0.09 0.09
500 (R#4)	0.43 0.47	0.39 0.39	0.24 0.17	0.09 0.08	0.09 0.06	0.06 0.06	BMDL BMDL	BMDL BMDL	0.11 0.09	0.08 0.08
800 (R#4)	0.48 0.41	0.40 0.42	0.17 0.17	0.21 0.20	0.06 0.06	0.06 0.05	BMDL BMDL	BMDL BMDL	0.09 0.09	0.08 0.08
0 (R#5)	0.47 0.46	0.34 0.35	0.08 0.07	0.07 0.07	0.06 0.05	0.05 0.05	BMDL BMDL	BMDL BMDL	0.08 0.08	0.08 0.08
300 (R#5)	0.47 0.48	0.39 0.41	0.06 0.07	0.18 0.17	0.05 0.06	0.05 0.05	BMDL BMDL	BMDL BMDL	0.08 0.08	0.08 0.08
500 (R#5)	0.44 0.41	0.35 0.41	0.06 0.06	0.16 0.17	0.05 0.05	BMDL BMDL	BMDL BMDL	BMDL BMDL	0.08 0.08	0.07 0.07
800 (R#5)	0.44 0.45	0.42 0.36	0.19 0.19	0.14 0.14	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	0.08 0.07	0.07 0.07

Table 13 (cont.). Recirculation Experiment - Reaction By-products as Determined by HPLC.								
Dose (krad)	Formaldehyde (mg L ⁻¹)		Acetaldehyde (mg L ⁻¹)		Acetone (mg L ⁻¹)		Glyoxal (mg L ⁻¹)	
	influent	effluent	influent	effluent	influent	effluent	influent	effluent
0 (R#1)	1.29 1.28	0.71 0.75	1.49 1.44	1.62 1.62	BMDL BMDL	BMDL BMDL	0.28 0.31	0.34 0.34
300 (R#1)	BMDL BMDL	BMDL BMDL	0.53 0.53	BMDL BMDL	BMDL BMDL	2.50 1.70	1.87 2.05	BMDL BMDL
500 (R#1)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
800 (R#1)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
300 (R#2)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
500 (R#2)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
800 (R#2)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
0 (R#3)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
300 (R#3)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
500 (R#3)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
800 (R#3)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
300 (R#4)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
500 (R#4)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
800 (R#4)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
0 (R#5)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
300 (R#5)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
500 (R#5)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL
800 (R#5)	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL	BMDL BMDL

Figure 6. Benzene concentration in full-scale recirculation experiment

Figure 7. Comparison of the gas chromatographic and high-performance liquid chromatography results of nitrobenzene concentration in the re-circulation experiment

Figure 8. Formation and decomposition of phenol during the recirculation experiment

Figure 9. Formation and removal of 2-nitrophenol during the recirculation experiment

Figure 10. Formation and removal of 4-nitrophenol during the recirculation experiment

Figure 11. Formation and removal of 2,4-dinitrophenol during the recirculation experiments

Figure 12. Formation and decay of formaldehyde during the recirculation experiment

Figure 13. Formation and decay of acetaldehyde during the recirculation experiment

Figure 14. Formation and decay of acetone during the recirculation experiment

Figure 15. Formation and decay of glyoxal during the recirculation experiment

Figure 16. Total Organic Carbon concentration throughout the recirculation experiment

Summary and Conclusions

Analysis of the data from the recirculation experiment with 3,000 gallons of simulated wastewater indicated that benzene, and resulting reaction by-products, can be reduced to federal discharge limits in less than five hours utilizing a dose of approximately 500 krad. Since the anticipated wastewater flow at SRL is 7,200 gallons per day (5 gpm), three 2,400 batches could easily be recirculated at 500 krad in less than 15 hours a day.

High energy electron beam irradiation appears to be a viable alternative for the destruction of benzene from the laboratory low-level mixed waste.

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SECTION IIA

**TEST OF ELECTRON-BEAM TECHNOLOGY ON SAVANNAH RIVER
LABORATORY LOW-ACTIVITY AQUEOUS WASTE FOR DESTRUCTION
OF BENZENE AND BENZENE DERIVATIVES**

QA/QC Project Plan Final Report

Submitted By:

Michael G. Nickelsen and William J. Cooper
Drinking Water Research Center
Florida International University
Miami, Florida 33199

Savannah River Laboratory

Project Number: D18642EE

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1.1 Quantitative Quality Assurance Objectives

TABLE 1-1. SUMMARY OF TARGETED QUANTITATIVE QUALITY ASSURANCE OBJECTIVES.

Measurement Parameter (Method)	Method Detection Limit (mg/L)	Precision Within Samples (RPD)	Precision Between Samples (RPD)	Accuracy (%R)	Completeness (%C)
Benzene (Static Headspace)	0.0001	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
Nitrobenzene (Static Headspace)	0.35	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
Nitrobenzene (HPLC)	0.02	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
<i>o</i> -Nitrophenol (HPLC)	0.04	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
<i>m</i> -Nitrophenol (HPLC)	0.02	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
<i>p</i> -Nitrophenol (HPLC)	0.01	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
2,4-Dinitrophenol (HPLC)	0.005	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
Phenol (HPLC)	0.01	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
Aldehydes (HPLC)	0.01	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%
Ketones (HPLC)	0.01	$< \pm 5\%$	$< \pm 10\%$	$\pm 10\%$	90%

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1.1 Quantitative Quality Assurance Objectives (cont...)

TABLE 1-2. SUMMARY OF EXPERIMENTAL QUANTITATIVE QUALITY ASSURANCE OBJECTIVES.

Measurement Parameter (Method)	Method Detection Limit (mg/L)	Precision Within Samples (RPD)	Precision Between Samples (RPD)	Accuracy (%R)	Completeness (%C)
Benzene (Static Headspace)	0.0001	< ±4%	< ±5%	± 3%	99%
Nitrobenzene (Static Headspace)	0.35	< ±1%	< ±5%	± 6%	100%
Nitrobenzene (HPLC)	0.02	< ±1%	< ±5%	± 2%	96%
<i>o</i> -Nitrophenol (HPLC)	0.04	< ±1%	< ±5%	± 2%	100%
<i>m</i> -Nitrophenol (HPLC)	0.02	< ±1%	< ±5%	± 3%	100%
<i>p</i> -Nitrophenol (HPLC)	0.01	< ±1%	< ±5%	± 2%	100%
2,4-Dinitrophenol (HPLC)	0.005	< ±1%	< ±5%	± 4%	100%
Phenol (HPLC)	0.01	< ±1%	< ±5%	± 2%	100%
Aldehydes (HPLC)	0.01	< ±1%	< ±5%	± 2%	100%
Ketones (HPLC)	0.01	< ±1%	< ±5%	± 3%	100%

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1.2 Discussion of Qualitative QA Objectives

1.2.1 Representativeness

Since both influent and effluent samples were collected at each irradiation dose, the data generated was representative of the effect of the actual electron beam process on essentially matched experimental material (i.e., volumes of simulated Savannah River low-activity aqueous waste).

1.2.2 Comparability

The results of the experiments are comparable to other studies using an electron beam of the same voltage (1.5 MeV), a weir water delivery system of the same design as at our facility, and performed under similar experimental conditions.

1.3 Discussion of How Not Meeting the QA Objectives Will Affect Decision Objectives

Each experiment will be conducted in a step wise manner. Once the electron accelerator is fully operational then the computer will be attached to the output of the RTDs and calibrated. The experiment will be completed and samples transported back to the laboratory for analysis. If the QA objectives of the experiment are not achieved, the experiment may be replicated as necessary to obtain data suitable for statistical data analysis. Therefore, no decisions will be made if the QA objectives are not achieved, but rather corrective action will be taken and additional data taken as required. As indicated in Tables 1-1 and 1-2 all QA objectives were met. Therefore replication of the experiment was not necessary.

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2.1 Sampling Procedures

2.1.1 Analyte (Hazardous Organic Compound) Sampling Procedure

All samples obtained in the ^{60}Co and full scale treatment studies were collected in EPA 40 mL PFTE-lined septum screw cap vials at each applied dose and both the influent and effluent sampling sites, respectively. Each sample was immediately chilled to 4 °C with ice.

2.1.2 General Water Characteristics Sampling Procedure

The parameters analyzed at both the influent and effluent are outlined in Tables 1-1 and 1-2 of the QA Narrative Statement.

2.1.3 Preparation and Cleaning of Sampling Equipment and Containers

All chemicals were of 99% purity or greater and were used without further purification. All organic sampling equipment and containers were thoroughly washed, solvent rinsed, and dried at 105 °C overnight prior to their use.

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ANALYTICAL PROCEDURES AND CALIBRATION

3.1 Standard Methods

All parameters were analyzed according to the reference methods cited in Tables 1-1 and 1-2 of the QA Narrative Statement.

3.2 Non-Standard Methods

3.2.1 Static Headspace for Benzene and Nitrobenzene

In order to determine the precision, accuracy, and detection limits of the various compounds, purged distilled water (PDW) was spiked with standard solution and analyzed.

3.2.2 HPLC for Nitrobenzene, Phenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, and 2,4-Dinitrophenol.

Many techniques have been employed in measuring trace amounts of phenols in water samples. The EPA method 604 provides two different GC methods for detecting these compounds. We have found, however, that HPLC provides a fast, sensitive method that requires no derivatization. This method is approved for analysis of drinking water and is the method used for our certification.

Nitrobenzene and various phenols were analyzed using a Hewlett Packard 1090M HPLC equipped with a 1040 diode-array detector. Separation takes place using a Hypersil 5 micron reverse-phase column (HP), 2.1mm x 100mm ID. The compounds were monitored by their absorbance at 280nm and were quantified by a Hewlett Packard series 300 computer against previously generated standard curves. The identities were confirmed by their UV spectra.

3.2.2 HPLC for Aldehydes and Ketones

Various aldehydes and ketones were analyzed using a Hewlett Packard 1090M HPLC equipped with a 1040 diode-array detector after derivitazition with 2,4-dinitrophenylhydrazine. Separation takes place using a Hypersil 5 micron reverse-phase column (HP), 2.1mm x 100mm ID. The resulting hydrazones were monitored by their absorbance at 370nm and were quantified by a Hewlett Packard series 300 computer against previously generated standard curves.

3.3 Calibration Procedures

The calibration procedures for all analyses were either EPA-approved or those listed in Standard Methods for the Examination of Water and Wastewater, 16th Edition, for the analytes to be studied.

TABLE 3-1. List of Standards, Including Source, Traceability, and Purity Checks

Standard	Source	Traceability	Purity Check
Benzene	Supelco	Lot Number	GC
Nitrobenzene	Supelco	Lot Number	GC HPLC
Phenol	Supelco	Lot Number	HPLC
2-Nitrophenol	Supelco	Lot Number	HPLC
3-Nitrophenol	Supelco	Lot Number	HPLC
4-Nitrophenol	Supelco	Lot Number	HPLC
2,4-Dinitrophenol	Supelco	Lot Number	HPLC
Formaldehyde	Supelco	Lot Number	HPLC
Acetaldehyde	Supelco	Lot Number	HPLC
Acetone	Supelco	Lot Number	HPLC
Glyoxal	Supelco	Lot Number	HPLC

3.3.1 Describe Frequency of Calibration Checks

A calibration check was performed every 20 samples.

3.3.2 Define Acceptance Criteria for all Calibration Measurements

An entire calibration curve will be dropped if the linear least squares correlation coefficient is less than 0.95. In addition, the precision between calibration checks must fall within 90 - 110% of the original calibration. All calibration curves utilized in this study fell within the two previously described criteria.

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DATA REDUCTION, VALIDATION, AND REPORTING

4.1 Data Reduction

4.1.1 Individuals Responsible

The Quality Assurance Coordinator and Supervisor were responsible for all data reduction. All principal project investigators have acted in this regard.

4.1.2 Summary of Statistical Approach for Reducing Data, Including Units and Definitions of Terms

Analysis of variance and regression techniques were used to analyze the data. The effects of electron dose, water quality, concentration and the presence or absence of other compounds on each compound tested were analyzed as a factorial experiment. Nonlinear regression analysis was used to fit curves relating change in concentrations to electron dose for each treatment combination found to differ in the analysis of variance.

Data reduction involved calculating the concentration mean and standard deviation of duplicate samples for both influent and effluent samples under a given set of experimental conditions. Both absolute ($\mu\text{g L}^{-1}$) and relative (%) change in concentration was calculated along with dose (krads) for that change.

4.1.3 Description of How Results on Blanks Will be Treated in the Calculations

All Samples were background corrected (blank corrected). In the event of blank contamination, the data set generated would have been dropped and the experiment repeated. No such condition existed.

4.2 Data Validation

4.2.1 Individuals Responsible

The Quality Assurance Coordinator and Supervisor were responsible for all data validation. All principal project investigators have acted in this regard.

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4.2.2 Procedures for Determining Outliers and Flagging Data

Data Identification Checks - all data was checked to ensure they were properly identified. The three identification fields which must be correct are time, location, and parameter. This information may be used to explain why no data are reported for a specific time interval, or it could be the basis for deleting data. All data generated conformed to the data identification criteria.

Unusual Event Review - a log was maintained to record such extrinsic events that could explain unusual data (e.g., power outages, changes in carrier gas flow rate, incorrect temperature programming of gas chromatographs, etc.). This information may be used to explain why no data are reported for a specific time interval, or it could be the basis for deleting data. No such condition existed.

Deterministic Relationship Checks - individual parameters were routinely checked to ensure that the measured values on an individual parameter did not exceed the corresponding measured control value. For example, benzene values at any irradiation dose should not exceed the value measured when no irradiation has been applied (i.e., all benzene values should be less than or equal to the control value). This was most easily accomplished by data plotting (See Final Report).

Tests for Historical Consistency - these tests check the consistency of the data set with respect to similar data recorded in the past. This was accomplished with the use of Shewhart Control Charts (Section 5.3.5).

4.3 Data Reporting

All analysts were responsible for reporting raw data to either the Supervisor or Quality Assurance Coordinator for data reduction and validation.

Figure 4-1. FLOWCHART OF THE DATA HANDLING PROCESS

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INTERNAL QUALITY CONTROL CHECKS

5.1 Samples

Triplicate samples were be collected for major analyses. Of the triplicate samples collected, two were used for the actual analyses while the remaining sample was held in reserve.

5.2 Spikes

5.2.1 Matrix Spikes and Matrix Spike Duplicates

A matrix spike was employed to provide a measure of accuracy for the method used in a given matrix. A matrix spike analysis was performed by adding a predetermined quantity of stock solutions of certain analytes to a sample matrix prior to sample extraction/derivatization and analysis. Spike recoveries must be 90-110% for the data to be acceptable. All data generated met this criteria.

5.2.2 Spiked Blanks

For each parameter tested, a reagent grade water spike was made and analyzed along with the samples. Spike recoveries must be 90-110% recovery for the data to be acceptable. All spike recoveries fell within the acceptable range.

5.2.3 Internal Standards

A known concentration of IS was injected into all samples, spikes, blanks and standards.

5.3 Other

5.3.1 Blanks

5.3.1.1 Field Blank

A field blank consists of reagent grade water that is as free of analyte as possible and is transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. A field blank was used for each experiment.

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5.3.1.2 Trip Blank

A trip blank consists of reagent grade water that is as free of analyte as possible and is transported to the sampling site and returned to the laboratory without being opened. A trip blank was used for each experiment.

5.3.1.3 Reagent Blank

A reagent blank consists of reagent grade water that is as free of analyte as possible and contains all the reagents in the same volume as used in the processing of the samples. The reagent blank is carried through the complete sample preparation procedure and contained the same reagent concentrations in the final solution as in the sample solution used for analysis. A reagent blank was used for each analysis date.

5.3.2 Control Charts

Dr. Walter A. Shewhart of Bell Telephone Laboratories developed the basis theory control charts in the 1920's. His book on statistical quality control grew out of this original work. Since then, industrial acceptance of these control chart concepts and other statistical techniques have refined and quantified the quest for quality in manufacturing. Although originally developed for control of production processes when large numbers of articles were being manufactured and inspected on an essentially continuous basis, these same concepts have been readily adopted to laboratory operations where the analyst produces comparatively fewer results on an intermittent basis.

As in the CuSum approach, precision control charts are prepared from duplicate data analyses and accuracy control charts are prepared from spiked data analyses. Once the control charts are constructed, however, data are plotted as individual values rather than cumulative sums.

Certain constants (factors) are also involved in the preparation of Shewhart Charts, depending upon how the data is grouped, the size of the grouping, and the type of control limit formulation calculation.

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FACTORS FOR COMPUTING CONTROL CHART LINES

Observations in Subgroup (σ)	Factor A_2	Factor D_4
2	1.88	3.27
3	1.02	2.58
4	0.73	2.28
5	0.58	2.12
6	0.48	2.00
7	0.42	1.92
8	0.37	1.86

Inherent in the Shewhart approach is recognition of the basic assumption that variations exist in every method. That is, no procedure is so perfect, so unaffected by its environment, that it will always give exactly the same assay value or product. Where such situations seem to exist, either the device used to measure the process is not sensitive enough or the person making the measurements is not performing properly. For our purposes, the recorded difference between paired samples should never be less than one-half the minimum detectable limit of the parameter under consideration. In the following outlines for preparing precision and accuracy control charts, nitrate data were used to develop the examples. Therefore, the minimum values shown are 0.05 (one-half the detectable limit of 0.1 mg L as N).

5.3.2.1 Precision Control Charts

These charts are developed by collecting data for many samples, a minimum of 15 to 20, run in duplicate under assumed controlled conditions. Once these data have been generated, preferable over an extended period of laboratory time, the following steps should be followed to construct the control chart:

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- a) List the range (R) for each set of samples. That is, the absolute value of the difference between each set of samples.

0.10	0.05	0.05	0.05	0.10
0.05	0.05	0.05	0.05	0.30
0.05	0.05	0.05	0.05	0.10
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05

- b) Calculate the average range (R_{avg}) by summing the list of R values and dividing by the number of sets of duplicates:

$$R_{avg} = \frac{\sum R}{\sigma}$$

$$\frac{2.15}{R_{avg} = 35} = 0.06$$

- c) Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4 R_{avg}$$

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where D_4 is a constant dependent on the number of units in the subgroup. In this case, since two observations are in the subgroup, $D_4 = 3.27$

$$UCL_R = 3.27 R_{avg} = 0.20$$

- d) Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2.3 (D_4 R_{avg} - R_{avg}) + R_{avg}$$

$$UWL_R = 0.15$$

This UWL corresponds to the 95% confidence level.

- e) Now graph R_{avg} , UWL_R and UCL_R in the following manner:

- f) The above precision control chart for nitrates is now complete, and can be used to plot R values on subsequent duplicate samples to determine if the system is in control, out of control (plotted R value beyond the UCL), and or detect any trends developing within the system.

1. In this example, a trend has developed between duplicate sample sets 4-7. Although the system is not out of control, all variables in the procedure should be checked in an attempt to stop this obvious trend before the UCL is reached.

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5.3.2.2 Accuracy Control Charts

As in the above system, these charts are developed by collecting data for many samples, a minimum of 15 to 20, but on spiked samples (preferably) or standards under assumed controlled conditions. Again, these data should be generated over an extended period of laboratory time, and be representative of normal operating conditions. The following steps should be followed to construct accuracy control charts:

- List the range (R) and the average (X) of each subgroup of data. Note: In the following example of nitrate data, subgroups of monthly data involving four (4) observations were used:

$$X = \frac{\sum d_{\text{Found} - \text{Actual}}}{n}$$

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Month	Actual	Found	R	X
Sept.	1.1	1.1	0	0
	1.1	1.1		
	1.1	1.1		
	1.1	1.1		
Nov.	1.1	1.1	0.1	-0.025
	1.1	1.1		
	1.2	1.1		
	1.2	1.2		
Oct.	1.0	1.1	0.1	0.025
	1.0	1.0		
	1.0	1.0		
	1.0	1.0		
Dec.	1.0	0.9	0.2	0
	1.0	1.0		
	1.0	1.1		
	1.0	1.0		

- b) Calculate the average range ($R_{\bar{a},g}$) by summing the list of R values and dividing by the number of subgroups:

$$R_{\bar{a},g} = \frac{\sum R}{\sigma}$$

$$\frac{0.40}{R_{\bar{a},g} = 4} = 0.10$$

- c) Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4 R_{\bar{a},g}$$

as in the precision control chart. In this case $D_4 = 2.28$

$$UCL_R = 2.28 R_{\bar{a},g} = 0.23$$

- d) Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2.3 (D_4 R_{avg} - R_{avg}) + R_{avg}$$

$$UWL_R = 0.19$$

- e) Now graph R_{avg} , UWL_R , and UCL_R in the following manner:

- f) Turning now to the X values, calculate the UCL_X by the formula:

$$UCL_X = A_2 R_{avg}$$

where A_2 is a constant dependent on the number of units in the subgroup. In this case, since four (4) observations are in the subgroup, $A_2 = 0.73$, therefore,

$$UCL_X = 0.73$$

- g) Calculate the UWL_X by the formula:

$$UWL_X = 2.3 A_2 R_{avg}$$

$$UWL_X = 0.05$$

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Note: Lower Warning Limit (LWL_x) and Lower Control Limit (LCL_x) are simply the negative values of UWL_x and UCL_x respectively.

- h) Now graph the standard Nominal Value (set equal to zero), UWL_x and UCL_x , LWL_x , and LCL_x in the following manner:

Both precision and control charts were constructed for each parameter analyzed and are listed in Appendix B. In situations where an out of control condition appeared, all data reanalyzed after the out of control situation was corrected (i.e., specifically for benzene during the ^{60}Co experiments).

Both completeness and method detection limit were calculated as described in Section 8 of the QA Narrative Statement and are listed in Tables 1-1 and 1-2.

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5.3.3 Calibration Standards

For each parameter tested no less than three (3), usually five (5), concentrations were used to generate a standard curve (calibration standards were be prepared in the type of aqueous matrix being studied). The parameter concentration was then calculated based on the slope of the resulting linear curve. If the curve is not linear in response appropriate measures are taken to correct the systems performance. One check standard was analyzed with each analytical batch or every 20 samples, whichever is greater, to assure there is no drift from the calibration curve.

5.3.4 Proficiency Testing of Analysts

Twice annually, the Drinking Water Research Center, is sent Quality Control samples by the United States Environmental Protection Agency for the parameters selected. In addition, the Drinking Water Research Center has requested other sets of Quality Control samples from the United States Environmental Protection Agency that are sent with know values. These values are kept secret from analysts and technicians who run the samples with no bias.

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APPENDIX A

Glossary of Terms

Biannually: Frequency over the period of one year equivalent to once every six (6) months.

95% Confidence Level: A sample which falls within the upper warning limits determined by the Mean Value $\pm$ 2 Standard Deviation units. Any sample which falls outside this value is discarded and repeated.

Control Limits: Used to monitor a measurement system's performance. The upper and lower control limits (UCL, LCL) are determined by the Mean Value $\pm$ 3 Standard Deviation units.

Duplicate Samples: Two or more aliquots obtained from a single sample. These are used to determine precision.

Field/Travel Blanks: Uncontaminated laboratory pure water is transferred to a sample bottle in the field under the same conditions the other field samples are collected. These blanks are used to assure the purity of any preservatives used and to check the technique of the sampler to control vectors of contamination. These blanks are analyzed with the field samples back at the laboratory.

Instrument Calibration: All instruments are calibrated for zero and span prior to analyzing samples.

Measurement Systems Blank: A sample with a concentration of zero for the measurement parameter of the system. This is used for all analyses and standardization procedures with the exception of pH and Temperature.

Proficiency Test Samples: Sample provided by USEPA with unknown concentrations of specific measurement parameters. Passing of these samples is required by HRS as part of the Environmental Water Testing Certification Program.

Quality Control Sample: A sample with a known concentration of a specific analyte that has been verified by analysis using the same measurement system (i.e. USEPA Quality Control Samples).

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Reagent Check: Any reagents with an expired shelf life, discoloration or poor performance are discarded and replaced.

Specialist: A person experienced in specific analytical procedures or methodologies.

Spiked Sample: Any sample altered by the addition of a compound of known concentration for the purpose of obtaining recovery data.

Split Samples: Two identical samples obtained by dividing one sample into two. Each is analyzed by a different operator or laboratory. These are used for intra- and inter- laboratory audits, respectively.

Standards: Analytically prepared reagents of known concentrations. These are used to standardize reagents, calibrate instruments and determine linear regression analysis.

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APPENDIX B

QA/QC Precision and Accuracy Control Charts

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Precision Control Chart

Accuracy Control Chart

Precision Control Chart

Accuracy Control Chart

Precision Control Chart

Accuracy Control Chart

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Precision Control Chart

Accuracy Control Chart

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SECTION IB

**TEST OF ELECTRON-BEAM TECHNOLOGY ON SAVANNAH RIVER
LABORATORY LOW-ACTIVITY AQUEOUS WASTE FOR INACTIVATION
OF BACTERIA**

Final Report
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Submitted By:

Charles N. Kurucz and Thomas D. Waite
University of Miami
Coral Gables, Florida 33124

Savannah River Laboratory

Project Number: D18642EE

Technical Representative: Dr. Jane Bibler
Principal Investigator: Dr. Roger Dougal

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1.0 INTRODUCTION

This report describes the work performed by the University of Miami as a subcontractor to the University of South Carolina under Contract Number: D18642EE, Test of Electron Beam Technology on Savannah River Laboratory Low-Activity Aqueous Waste for Destruction of Benzene, Benzene Derivatives and Bacteria. The object of this contract was to determine whether and to what extent, organic contaminants (specifically benzene, nitrobenzene, phenol and nitrophenol) and microorganisms can be removed from a low-activity waste stream using the process of electron beam irradiation.

The specific objective of the work described herein was to determine the effectiveness of ionizing radiation on the inactivation of actual microbial pollutants, indicated in this report by LLW1 and LLW2, found in low level waste from the Savannah River Laboratory (SRL). Both bench scale scoping studies using ^{60}Co gamma irradiation and full scale studies using a 1.5 MV, 50 mA, 120 gpm electron beam treatment system at the Miami Electron Beam Research Facility (EBRF) were performed.

The studies were conducted utilizing the SRL bacteria and two surrogates, *Pseudomonas aeruginosa* and *Methylobacterium radiotolerans*. These surrogates were selected because it was uncertain as to whether enough actual SRL bacteria could be obtained/cultured to perform all of the bench and pilot scale experiments and to further indicate the effectiveness of the process. *Pseudomonas* sp. were selected because they are the most probable microbes of interest to be found in the SRL waste based on characterizations of waste streams at other SR plants, and what is generally expected to be present in similar waste treatment situations. *Methylobacterium radiotolerans* was selected because of resistance to the effects of ionizing radiation.

In the bench scale experiments water containing one of the micro-organisms was subjected to gamma irradiation by a ^{60}Co source in order to characterize the inactivation efficiency as a function of water quality and irradiation dose. The specific micro-organisms,

solution makeup, and analytical protocols used are described in the detailed test plans presented in Appendix A. Pilot scale experiments were performed at the Electron Beam Research Facility (EBRF) to determine the inactivation efficiencies of SRL bacteria and *Pseudomonas aeruginosa* as a function of irradiation dose. The detailed test plan which was followed is also presented in Appendix A.

2.0 METHODS AND MATERIALS

2.1 Laboratory Procedures

Cultures of *Pseudomonas aeruginosa* and *Methylobacterium radiotolerans* were obtained from the American Type Culture Collection (#90-04SV: #88-11). Nutrient broth was added to the pellets in the original bottles and after approximately thirty seconds, this mix was added to a sterile test tube containing 5 ml of nutrient broth. This mixture was incubated for several days at 37° C and the temperature of the incubator was checked daily by an NIST thermometer. Periodically, a sterile inoculating loop was dipped into the mixture and scraped onto a sterile agar plate, which was also incubated under conditions appropriate for the particular bacteria. LLW samples were obtained from non radioactive waste streams at SRL and grown on agar slants. Colonies from the slants were streaked on plates and were incubated at 37° C. As individual colonies appeared on the plates, they were transferred onto fresh agar plates. Some were also innoculated into sterile nutrient broth for harvesting. Additionally, colonies were lifted and kept as standards on agar slants. Nutrient broth and Nutrient agar were obtained from Difco (#799217: #792266).

For all experiments, sterile nutrient broth was prepared by mixing 8 g nutrient broth with 1 liter of distilled water. This was then autoclaved for 15 minutes at 250° F and 14 psi. The temperature of the autoclave was checked every five runs by a NIST thermometer. Also, nutrient agar was prepared by mixing 23 g of nutrient agar with 1 liter distilled water and autoclaving 15 minutes. Agar plates were prepared by pouring the sterile agar solution into sterile disposable petri dishes and the dishes were then placed in the refrigerator upside down. Each plate had an agar thickness of approximately 2 mm to 4 mm.

To harvest bacterial cells, 250 ml flasks were filled with 200 ml of nutrient broth and autoclaved for 15 minutes. These flasks were allowed to cool to room temperature. Two colonies were lifted from the culture plates and placed in each flask. These flasks were then placed on an incubator shaker at 200 rpm and the appropriate temperature (37° C for *Pseudomonas aeruginosa* and 26° C for *Methylobacterium radiotolerans*) for the appropriate

time (24 hours for *Pseudomonas aeruginosa* and 72 hours for *Methylobacterium radiotolerans*). A blank flask containing only sterile nutrient broth was included on the shaker to detect contamination.

At the end of this time, the broth was removed from the incubator-shaker and poured into sterile centrifuge tubes. These tubes were placed into a centrifuge and spun at 10,000 rpm for 10 minutes. Upon completion, excess broth was poured off a compact pellet of bacteria in the bottom of the tube, and sterile distilled water was added to resuspend the bacteria. The bacteria were washed three times. Excess water was drained from the tubes and 10 ml of sterile distilled water was then added. The bacteria were mixed into this water with a sterile rod and this mixture was poured into a sterile plastic stoppered vial and refrigerated. This mixture was used for the samples to be irradiated.

2.2 Bench Scale Experiments

To prepare irradiation samples, excess volumes of the test mix (or distilled water) to be used were autoclaved in 100 ml volumetric flasks. Various dilutions of bacteria were used to achieve a target concentration in the samples. For example, for a 1:100 mix, one ml of the bacteria mixture would be added to 99 ml of mix or distilled water. This mixture was then shaken and added in 20 ml increments to sterile sample bottles. This volume fills the bottles approximately half-way and allows for mixing by shaking prior to irradiation. These samples were then refrigerated until irradiation, which was normally conducted using two or three doses. A trip blank of sterile distilled water and a quality control sample of *Pseudomonas aeruginosa* was also transported during irradiation.

The bench scale irradiations were conducted using a 5000 Curie ^{60}Co gamma source located at the University of Miami School of Medicine. The samples were placed at the appropriate distance from the source for a specific amount of time to apply a particular dose. After irradiation, samples were immediately diluted in a 10 mg/L sodium thiosulfate solution. The samples were then refrigerated and transported back to the laboratory for analysis.

Enumeration of viable bacteria in the samples was accomplished by dilution and plating on nutrient agar. The zero dose samples were diluted to 10^{-6} , which was performed by shaking the original sample on a vortex mixer, removing 1 ml of the sample and adding it to a test tube containing 9 ml of sterile distilled water. This was repeated five times. The irradiated samples were plated directly from the samples and from the first dilution tube

To plate the diluted samples, 0.1 ml was removed from each dilution tube using a sterile pipet and deposited onto a sterile agar plate. This was then spread by spinning the plate in contact with a sterile plating instrument. Three plates were prepared for each dilution tube. The process was repeated for the irradiated samples, yielding three plates from each of the sodium thiosulfate tubes and three plates directly from each sample. These plates were then placed upside down in an incubator at the appropriate temperature for the appropriate time (depending on the bacteria to be enumerated).

After incubation, colonies on the plates were counted, and an individual colony was assumed to represent one cell from the original sample. Plates from all samples were counted and an average of the three platings from a particular dilution was calculated. A plate containing 10 to 300 colonies may be considered significant for estimates of population in the original sample. The populations from the zero-dose samples and the irradiated samples may then be compared. A target population of 10^5 to 10^6 cells/ml was ideal. Cultures of *Pseudomonas aeruginosa* and the low level waste were typically counted after 24 hours. Colonies of *Methylobacterium radiotolerans* were counted after 72 hours and again at 168 hours, due to slower rates of growth. After the counting was completed, the contaminated plates were autoclaved for 15 minutes to eliminate any residual biological activity before disposal.

2.3 Full Scale Experiments

Full scale experiments were conducted at the Electron Beam Research Facility at the Virginia Key Wastewater Treatment Plant, utilizing a horizontal 1.5 MeV insulated-core

transformer (ICT) electron accelerator, a water delivery system, and ancillary equipment.

It was estimated through laboratory procedures that harvesting bacteria in 20 liters of broth would provide an adequate bacterial population for a 4600 gallon sample of the simulant Mix #32 (See Table 1) at a pH of 5.0. The nutrient broth was prepared by adding 8.0 grams nutrient broth per liter of distilled water. The broth was distributed into nine 2000 mL flasks, each containing about 1800 ml of broth and a magnetic stir bar. The remainder of the 20 liters were placed in 250 ml flasks. These containers were then autoclaved for 15 minutes at 250° F and 14 psi. Upon cooling, the flasks were inoculated with colonies of the appropriate bacteria following aseptic techniques. The 2000 ml flasks were then mixed for at least 24 hours. The 250 ml flasks were placed on an incubator shaker for the same amount of time. At the end of the incubation period the broth appeared dense as the bacteria were harvested. For each experiment roughly 6 of the 20 liters of broth were centrifuged at 10,000 rpm for 10 minutes. The clean bacteria were then suspended in distilled water and refrigerated until the time of the experiment. The remaining broth plus bacteria was poured directly into the tanker before the experiment.

Two days prior to the experiment, all of the lines in the system were flooded with a mix of water and Clorox bleach which was left until the day of the experiment. Approximately 3/4 of a gallon was used for the 100 gallons in the system. Also, the tanker was then cleaned using a 1000 psi pressure cleaner.

The following amounts of chemicals were required to achieve the test conditions for a 4600 gallon sample: (1) 400 grams of sodium thiosulfate, (2) 21 kilograms of sodium nitrate, (3) 10 kilograms of sodium sulfate, (4) 43 kilograms of potassium dihydrogen phosphate, (5) 500 grams of ferrous chloride, (6) 18 kilograms of Alconox, and (7) 12.5 liters of concentrated hydrochloric acid. The chemical addition was performed as the tank filled to facilitate mixing, beginning when the tank was approximately half full.

Before the experiment, the lines were flushed with tap water to expel the residual

chlorine, and a base line chlorine concentration of 2.8 mg/L was reached before proceeding with the experiment. The tanker was then filled with the chemicals described above. Concentrated hydrochloric acid was then added to adjust the pH to 5.0. This was allowed to mix while the pH was being monitored. At this point, the residual chlorine was checked to confirm zero residual. Blank samples were then taken from the tanker and the lines to confirm low microbial activity.

Bacterial cultures were then added to both ports of the tanker to allow complete mixing. This was allowed to mix for 20 minutes before a tank sample was taken. The system was then operated at a flow of 100 gpm, and influent and effluent samples were taken for doses of 0, 50, 100, and 150 krad. Influent samples were immediately diluted into distilled water and the effluent samples were immediately diluted into 10 mg/L sodium thiosulfate solution.

These samples and tubes were then refrigerated until the completion of the experiment, and then transported back to the lab in a cooler. Finally, the appropriate dilutions were performed and plated according to the pour plate method (Standard Methods # 9125B). The plates were incubated at 32° C for 24 hours before being counted.

2.4 Quality Control

During the bench scale activities, quality control measures were considered. With each set of samples to be irradiated, a sample of *Pseudomonas aeruginosa* was also irradiated to ensure consistency of results. This culture was selected because it had been studied from the beginning of the experiment. A trip blank of distilled water and/or the appropriate solution was carried during transport of samples and plated for contamination. A sample of sterile nutrient broth was kept in the incubator-shaker during harvesting and plated for contamination. Sterile agar plates were kept in the incubator to confirm sterile conditions. Also, a sample of the dilution water was plated to confirm sterile conditions in the dilution process.

All studies have been performed in accordance with the Calibration Procedures and QA/QC plan presented in Appendixes B and C.

3.0 RESULTS AND DISCUSSION

3.1 Bench Scale Experiments

Initial studies were conducted at the ^{60}Co gamma irradiation facility using three selected surrogates of SRL waste, *Pseudomonas aeruginosa*, *Methylobacterium radiotolerans*, and LLW1. The inactivation of the bacterial species was studied in Mix #1, buffered distilled water and Mix #32. Mix #32 contained the following additives: 200 mg/L TOC as Alconox, 900 mg/L NO_3^- ion, 390 mg/L SO_4^{2-} ion, 1740 mg/L PO_4^{3-} ion, and 10 mg/L Fe^{2+} , and is a simulant of actual SRL waste. The doses selected were 100, 200, 300, and 500 krad, and the initial concentrations of bacteria were targeted at 10^5 to 10^6 ml^{-1} for all three surrogates. Three to four logs of removal of the bacterial population was observed when the appropriate species were exposed to the radiation doses in buffered distilled water (Mix #1) and Mix #32 as shown in Figures 1 through 6.

The initial level of bacteria was obtained by harvesting bacteria from sterile nutrient broth after incubation for 24 hours at 37°C on an incubator shaker at 200 rpm. This bacterial population was then centrifuged at 10,000 rpm for ten minutes at 4°C , and washed repeatedly with buffered distilled water. These were then resuspended in 10 ml of buffered distilled water. These were further diluted in Mix #1 or Mix #32 as appropriate to achieve the desired concentration.

During these initial experiments several changes were made to the test protocol as follows:

- 1) The dose administered was reduced to between 100 krad and 200 krad due to high levels of inactivation observed at 300 krad and 500 krad.
- 2) *Methylobacterium radiotolerans* were harvested in sterile nutrient broth for 72 hours at 26°C on an incubator-shaker at 200 rpm. This length of harvesting yielded higher populations than a length of 24 hours.

3) *Methylobacterium radiotolerans* bacterial colonies were counted after plating the samples and appropriate dilutions on triplicate sterile agar plates with incubation at 26° C for 72 to 168 hours. A longer incubation time was required for the *Methylobacterium radiotolerans* due to it's significantly slow growth with time.

The initial population of bacteria was in the range of 10^5 to 10^6 ml⁻¹ in Mix #1. For Mix #32, initial concentrations were in the range of 10^3 to 10^4 ml⁻¹ for LLW1 and *Methylobacterium radiotolerans*. The analysis of the irradiated samples was done by diluting the samples immediately in 10 mg/L sodium thiosulfate, and plating them in triplicate. The sodium thiosulfate was used to quench any further reaction oxidants produced by irradiation with the microbes during the time between collection of samples and plating.

All three bacteria were irradiated in Mix #2, Mix #3, and Mix #7. Mix #2 was a solution containing 200 mg/L TOC as Alconox. Mix #3 was a solution containing 900 mg/L NO₃⁻, and Mix #7 is a combination of the two. A summary of the make-up of the various mixes is presented in Table 1. Nearly complete inactivation was observed for all bacteria except *Methylobacterium radiotolerans* as shown in Figures 7 through 9.

Table 1: Experimental factors and concentrations for selected screening experiments to determine microbial inactivation efficiency for 10 ⁵ L ⁻¹ target populations.	
Mix	Constituents
# 1	Distilled water
# 2	200mg L ⁻¹ TOC (as ALCONOX™)
# 3	900mg L ⁻¹ NO ₃ ⁻
# 7	200mg L ⁻¹ TOC, 900NO ₃ ⁻
#32	200mg L ⁻¹ TOC, 900NO ₃ ⁻ , 390SO ₄ ⁻ ,1740PO ₄ ⁻³ , 10Fe ²⁺

In preparation for the full scale electron beam experiments which would use Mix #32, another experiment was performed using the surrogates *Pseudomonas aeruginosa* and LLW2 bacteria provided by SRL. For this experiment, Mix #32 was prepared with potable water to be more representative of the full scale experiments. The results are presented in Figure 10. A summary of the data from the bench scale studies is given in Tables 2 and 3.

3.2 Full Scale Experiments

The full scale experiment yielded high levels of inactivation of both *Pseudomonas aeruginosa* and LLW2. Initial concentrations of *Pseudomonas aeruginosa* averaged 8.48×10^5 and initial concentrations of LLW2 averaged 5.64×10^4 . Nearly complete inactivation of both cultures was observed at 150 krad as shown in Figure 11. These results correlate with the bench scale experiments conducted with Mix #32 when made with dechlorinated tap water at pH = 5.0. The inactivation, however, appears to be somewhat better with the gamma radiation. The data for the full scale experiments are given in Table 4.

The results of fitting the model

$$\text{Log (E/I)} = kD$$

where

E = Effluent population of bacteria (count ml⁻¹)

I = Average Influent population of bacteria

D = Dose (kilorads),

to the full scale data are given in Figure 12. From these curves it can be seen that a dose of approximately 250 kilorads should result in a 6 Log reduction in LLW2 bacteria.

3.3 Other Experiments

Several experiments to determine the time effects of the simulant Mix #32 on the *Pseudomonas aeruginosa* and LLW2 bacteria were also conducted. The results are given in Figure 13, Table 5 and Table 6. The results show no significant time change within the 1½ to 1 1½ hour time periods generally required to handle and stabilize in radiated and non-irradiated samples. The results of quality control plate counts are also shown in the control chart presented in Figure 14.

Inactivation of *Pseudomonas Aeruginosa* and LLW1 Set #1

Figure 1

Inactivation of *Pseudomonas* sp. and LLW1 by Radiation

Set #2

Figure 2

Inactivation of *Pseudomonas* sp., LLW1, and *Methylobacterium* sp. by Radiation

Set #1

Figure 3

Inactivation of *Pseudomonas* sp., LLW1, and *Methylobacterium* sp. by Radiation

Set #2

Figure 4

Inactivation of *Pseudomonas* sp., LLW1, and *Methylobacterium* sp. by Radiation

Set #1

Figure 5

Inactivation of *Pseudomonas* sp., LLW1, and *Methylobacterium* sp. by Radiation

Set #2

Figure 6

Inactivation of *Pseudomonas* sp. by Radiation

■ Mix #1 — Mix #3 — Mix #7

Figure 7

Inactivation of *Methylobacterium* sp. by Radiation

Figure 8

Inactivation of LLW1 by Radiation

Figure 9

BENCH SCALE EXPERIMENT

Dechlorinated Tap Water-pH 5

Figure 10

FULL SCALE EXPERIMENT *Pseudomonas Aeruginosa* and LLW2

Figure 11

Full Scale Electron Beam Fitted Results in Simulant Wastewater

Figure 12

Effect of Exposure to Mix #32 on *Pseudomonas Aeruginosa* and LLW2

Figure 13

Figure 14

Tables 2: Summary of Bench Scale Disinfection Experiments

Bacteria	Mix	Date	Dose				
			0	100	200	300	500
Pseudomonas	1	10/16/92	1.15E07	4.00E02	1.03E04	7.00E02	1.55E03
	1	10/22/92	1.91E07	3.25E03	1.50E01	1.00E00	1.00E00
	32	11/4/92	2.73E07		2.40E03		
	1	11/10/92	5.10E07	7.00E02	3.00E02		
	32	11/30/92	8.70E07	1.00E02	5.00E02		
	1	12/1/92	7.70E07	1.00E02	7.00E02		
	1	2/3/93	2.12E07	1.00E00	1.00E00	1.00E00	
	3	2/3/93	1.20E07	1.00E00	1.00E00	1.00E00	
	7	2/3/93	2.20E03	1.00E00	1.00E00	1.00E00	
LLW1	1	10/16/92	4.34E06	8.50E02	5.20E03	5.20E03	2.50E02
	1	10/22/92	7.72E06	1.80E02	6.00E01	2.00E01	1.00E01
	32	11/4/92	5.50E03		1.00E00		
	1	11/10/92	3.00E05	3.00E02	4.80E03		
	32	11/30/92	3.00E03	9.00E02	2.20E03		
	1	12/1/92	5.90E06	1.60E03	5.00E02		
	1	2/3/93	9.10E06	1.00E00	1.00E00		
	2	2/3/93	4.10E07	1.00E00	1.00E00		
	3	2/3/93	8.20E07	1.00E00	1.00E00		
	7	2/3/93	2.20E07	1.00E00	1.00E00		
Methylobacterium	32	11/4/92	4.30E03		1.00E00		
	1	11/10/92	2.00E05	3.68E04	1.39E04		
	32	11/30/92	2.70E05	5.30E03	2.00E03		
	1	12/1/92	3.00E05	5.34E04	2.90E03		
	2	2/3/93	1.27E04	3.29E03	8.60E02	9.00E01	
	3	2/3/93	1.98E06	3.69E04	4.20E03	2.00E02	
	7	2/3/93	4.90E03	7.00E02	4.00E02	1.00E02	

Table 3: Bench Scale Experiments with Mix #32 in Dechlorinated Potable Water of pH = 5	
Bacteria _{Dose}	Population/ML
PS ₀	9.87 E ⁻⁵
PS ₅₀	3.0 E ⁺¹
PS ₁₀₀	1.7 E ⁺¹
PS ₁₅₀	<10
LLW ₀	5.4 E ⁻⁶
LLW ₅₀	<10
LLW ₁₀₀	<10
LLW ₁₅₀	<10

Table 4: Results of Full Scale Disinfection Experiments					
Bacteria	Sample	Dose			
		0	50	100	150
Psuedomonas	Influent	8.0E05	8.5E05	7.8E05	9.3E05
	Effluent	8.5E05	1.6E02	3.0E01	3.0E01
LLW2	Influent	9.8E04	4.2E04	5.8E04	4.9E04
	Effluent	5.6E04	2.1E04	5.0E01	3.0E01

Table 5: Time Effect of Mix #32 in Distilled Water	
Bacteria _{Time}	Population
PS ₀	4.2 E ⁻⁶
PS ₃	4.3 E ⁻⁶
PS ₆	2.3 E ⁻⁶
PS ₉	2.5 E ⁻⁶
LLW ₀	4.3 E ⁻⁵
LLW ₃	1.2 E ⁻⁵
LLW ₆	1.3 E ⁻⁶
LLW ₉	6.3 E ⁻⁵

Table 6: Time Effect of pH 5 and Mix #32	
Bacteria _{Time}	Population
PS ₀	7.67 E ⁻⁶
PS ₃	6.13 E ⁻⁶
LLW ₀	5.97 E ⁻⁵
LLW ₃	8.00 E ⁻⁵

4.0 CONCLUSIONS

Both the bench scale and full scale studies have confirmed that electron beam irradiation can be used to effectively inactivate bacteria common to SRL waste in the presence of high TOC, nitrate, sulfate, phosphate and metals. The data show that a dose of 250 kilorads should be sufficient to inactivate almost all of the anticipated bacteria. If electron beam treatment is placed before any process filters the growth of bacteria on the filters would be minimized. Since the target density of 10^5 organisms/ml used in this study was based on SRL samples taken near process filters, the 250 kilorad dose might totally inactivate the smaller numbers of bacteria which would be expected upstream of the filters

It should be noted that the above dose is well within the treatment regime required to handle the removal of the anticipated organic chemicals investigated under separate contract by Florida International University. Analysis of the data from their full scale electron beam recirculation experiment with 3,000 gallons of simulated wastewater (Mix #32) indicates that benzene, and resulting by-products, can be reduced to federal discharge limits in less than five hours utilizing a dose of approximately 500 kilorads. Since the anticipated wastewater flow at SRL is 7,200 gallons per day (5 gpm), three 2,400 gallon batches could easily be recirculated at 500 kilorads in less than 15 hours each day. At this higher dose, complete inactivation of any bacteria is highly probable.

APPENDIX A

TEST PLANS

Test Plan #SRL-B1-Ver 1.0-920-609
⁶⁰Co Scoping Measurements
Inactivation of Microbial Pollutants

The most probable microbes of interest to be found in the SRL waste are *Pseudomonas* Sp. Specifically, gram negative aerobic rods and cocci (Part 7 in Bergey's Manual of Determinative Bacteriology) in concentrations of at least 10^5 mL^{-1} . This is based on characterizations of other waste streams at other SR plants, and what is generally expected to be present in similar waste treatment situations. It is anticipated that actual SRL waste with high concentrations of bacteria will be provided by SRL for use in the proposed experiments which follow. Since it will probably prove infeasible to obtain/culture enough actual SRL bacteria to perform all of the bench and pilot scale experiments, it will be necessary to select surrogates. For this reason it is recommended that a microbial characterization of the SRL waste stream be performed before bench testing begins and the results used to select two surrogate bacteria readily available from commercial sources.

The primary mechanism of microbial inactivation using radiation is the reaction of the radical species produced in water with the constituents of the microbes. The major factors that have been identified as affecting electron beam induced radical production in the mixed laboratory waste are nitrate and total organic carbon. However, because of the high concentration of sulfate and phosphate ions, and some heavy metals, additional factors will be screened. The weighted average of nitrate appears to be approximately 900 milligrams per liter. The TOC resulting from the use of soaps is approximately 200 milligrams per liter. The sulfate ion and phosphate ion weighted averages are 390 and 1740 mgL^{-1} , respectively.

Initial studies will be conducted at the ⁶⁰Co gamma irradiation facility utilizing SRL bacteria and two selected surrogates. Initial concentrations of bacteria will be targeted at 10^5 mL^{-1} for all three bacteria "types". For the SRL bacteria, the above variables will be examined in a full factorial design at two levels, 0 and the weighted average concentration of each factor, i.e. a $2 \times 2 \times 2 \times 2 \times 2$, as shown in Table 1. A full factorial design utilizing only TOC and NO_3^- will be used for the two surrogates to provide a comparison to the SRL bacteria under varying conditions.

Table 1. Experimental factors and concentrations for screening experiments to determine microbial inactivation efficiency for 10^5 mL⁻¹ populations.

Factors	Concentration (mg L ⁻¹)	
TOC	0	200
NO ₃ ⁻	0	900
SO ₄ ⁻²	0	390
PO ₄ ⁻³	0	1740
Metals	0	10

The experiments will be conducted in distilled water and the pH will be adjusted using hydrochloric acid. Nitrate will be added as NaNO₃. The anions will be added as either a sodium or potassium salt and the TOC will be added as Alconox. SRL bacteria will be cultured on normal nutrient broth. They will be harvested by centrifuging and washing the cells. The harvested bacteria will be resuspended in previously prepared media defined by each of the 32 water quality treatment combinations described above. Each treatment combination will be irradiated at 2 doses, 0 and 1000 krads, yielding a total of 32 vials to be irradiated and 32 control vials.

Viable bacterial populations will be determined by standard plate counts using the Pour Plate Method (Standard Methods #9125B). The determinations will be done in pairs (control and corresponding irradiated sample) and in random order to avoid any confounding of irradiation effects with time.

The dose actually delivered to the samples will be verified by including two vials of Fricke dosimeter solution which will be analyzed with a spectrophotometer to estimate the total dose received by the sample vials. A preliminary experiment will also be conducted by irradiating two vials of Fricke solution at each of the 10, 20, 30, and 40 cm circles for two time periods, 3 and 5 hours. The actual measured adsorbed doses will be compared to values calculated using several empirical and theoretical models relating time, distance and dose. See attached sample calculations for a 7 cm diameter bottle with .37 cm thick walls, placed 10 cm from a point source as measured to the closest point on the bottle, for a period of 120 minutes. The dose received by water on the near side of the bottle is 632.74 krads and on the far side 404.26.

Test Plan #SRL-B1-Ver 1.1-930314
⁶⁰Co Scoping Experiments
Inactivation of Microbial Pollutants

Bench scale ⁶⁰Co were initially conducted for selected combinations (Mix#1 and Mix #32) of the chemical constituents in simulated SRL low-level waste enumerated in version 1.0 of this plan. It was not feasible to run all 32 combinations of constituents as originally planned because of the considerable efforts required to obtain consistently good plate counts. In addition, because of differences between results for the surrogate bacterium *Pseudomonas* (PS) and sample bacteria similar to that found in the low-level waste (LLW1), a radiation resistant surrogate bacterium, *Methylobacterium radiotolerans* (RR), was obtained and preliminary experiments performed as described in Reports #1 and #2. The resulting procedures for processing these bacteria are described in Report #3.

Experiments with additional combinations of constituents (Mix #2, #3 and #7) were then performed with the intent of evaluating the effects of the most prevalent radical scavengers. Samples of actual SRL low-level waste bacteria (LLW2) were also received and experiments performed using Mix #1, #2, #3 and #7. The following preliminary conclusions were drawn:

1. The surrogate *Pseudomonas* bacterium (PS) behaved similar to the sample low-level waste bacteria (LLW1), but was less resistant to radiation than LLW1 in distilled water.
2. The radiation resistant surrogate *Methylobacterium radiotolerans* (RR) was more resistant to radiation than LLW1 in distilled water.
3. The PS bacterium was less radiation resistant than the RR bacterium, which in turn was less radiation resistant than LLW1 in Mix#32.
4. There were no differences in the inactivation of PS and RR bacteria between Mix#1 and Mix#32, however, inactivation of LLW1 was better in Mix#1 than Mix#32.
5. Mix #32 possibly kills LLW1 without radiation.
6. Alconox™ might kill PS and RR but NO₃⁻ does not appear to affect inactivation.
7. Removal of actual SRL low-level waste bacteria (LLW2) does not appear to be

affected by Alconox or NO_3^- . However, LLW2 is much less resistant than LLW1 in the presence of Alconox and /or NO_3^- .

- 8 Since LLW2 is much less resistant than LLW1, PS will be used as the surrogate in the E-beam experiments instead of the RR bacterium. The latter is too resistant (see 2, 3 and 7 above) and also more difficult to work with than PS (see Report #3)

Based on these conclusions the following experiments are proposed to complete the bench scale studies:

1. Suspension of a uniform mixtures of PS and LLW2 bacteria in potable water from the E-beam facility and simulated SRL wastewater (Mix #32 using potable water instead of distilled water). The seeded simulated SRL wastewater is to be split into three sets of sample vials. The vials will not be irradiated but will be plated after "0", 3, 6 and 9 hours, respectively, during which time they will be placed in a cooler as appropriate to simulate the normal handling of samples. The residual chlorine in the potable water will first be neutralized using sodium thiosulfate.

The purpose of this experiment is to determine the extent to which the simulated wastewater itself inactivates the bacteria. This information will be used to estimate the initial seeding requirements of the full scale E-beam experiments and to provide the basis for adjusting the results of irradiations.

2. PS and LLW2 bacteria in simulated SRL wastewater (Mix #32) to be irradiated at 50, 100, and 150 kilorads. The purpose of this experiment is to establish a correlation between surrogate and actual SRL bacterial inactivation in simulated SRL wastewater. This information will allow the extrapolation of full scale E-beam experiments with PS to LLW2 in the event that it is not possible to culture enough LLW2 for a full scale test.

Table 1. Experimental factors and concentrations for selected screening experiments to determine microbial inactivation efficiency for 10^5 L^{-1} target populations.

<u>Mix</u>	<u>Constituents</u>
#1	Distilled water
#2	$200\text{mg L}^{-1}\text{TOC}$ (as ALCONOX TM)
#3	$900\text{mg L}^{-1}\text{NO}_3^-$
#7	$200\text{mg L}^{-1}\text{TOC}$, 900NO_3^-
#32	$200\text{mg L}^{-1}\text{TOC}$, 900NO_3^- , 390SO_4^{2-} , 1740PO_4^{3-} , 10Fe^{2+}

Test Plan #SRL-B2-Ver 1.0-930314
Full Scale Electron Beam Experiments
for
Inactivation of Microbial Pollutants

Based on the bench scale ^{60}Co tests conducted for selected combinations of the chemical constituents in simulated SRL low-level waste enumerated in Test Plan #SRL-B1-Ver 1.0-920615 and #SRL-B1-Ver 1.1-930314, the surrogate bacterium *Pseudomonas aeruginosa* (PS) and actual bacteria from SRL low-level waste (LLW2) are proposed for full scale electron beam irradiation. Each bacterium will be seeded in a tanker containing at least 3,000 gallons of potable water to which 200mgL^{-1} TOC, 900mg L^{-1} NO_3^- , 390mgL^{-1} SO_4^{2-} , 1740mgL^{-1} PO_4^{3-} , and 10mgL^{-1} Fe^{2+} (Mix #32) have been added. An appropriate amount of sodium thiosulfate will also be added to neutralize the residual chlorine in the potable water. Enough bacteria will then be added to generate an initial count of approximately 10^5 L^{-1} . Although attempts are currently underway to culture enough LLW2 bacteria to seed at this level it is uncertain whether sufficient quantities can be obtained. Bench scale data will be available to extrapolate from the full scale PS experiment if necessary.

Both proposed full scale experiments will be conducted at the Electron Beam Research Facility (EBRF) and employ a 4,600 gallon tanker that will be filled with at least 3,000 gallons of potable water seeded with the appropriate bacterium. This simulated waste stream will then be pumped through the E-beam at approximately 100 gallons per minute. The choice of at least 3,000 gallons represents a balance between the need for larger numbers of bacteria and the amount of time to empty the tanker. Prior to filling and seeding, the tanker will be washed with AlconoxTM. An AlconoxTM mixture will also be pumped through the system to disinfect the lines and weir prior to conducting the experiment. A test wash will be performed to estimate the degree of disinfection and to estimate the residual concentration of AlconoxTM. The amount of AlconoxTM added during a full scale experiment to obtain the 200mgL^{-1} TOC will be reduced by the estimated residual from the washing test.

The experiments will be conducted in potable water and the pH will be adjusted to 3 using hydrochloric acid. Nitrate ion concentration will be adjusted using NaNO_3 . Sulfate ion concentration will be adjusted using Na_2SO_4 . Phosphate ion concentration will be adjusted using KH_2PO_4 . Fe^{2+} ion concentration will be adjusted using FeCl_2 . TOC will be added as AlconoxTM soap. Each experiment will be conducted at 4 doses, 0, 50, 100 and 150 krad. Sampling will take place as follows during an experiment.

<u>TIME(mins.)</u>	<u>ACTIVITY</u>
0	Take influent zero dose sample
1	take effluent zero dose sample
1-2	To 50 krads
6	Influent sample
7	Effluent sample
7-8	To 100 krads
12	Influent sample
13	Effluent sample
13-14	To 150 krads
18	Influent sample
19	Effluent sample
19-20	To 100 krads
24	Influent sample
25	Effluent sample
25-26	To 50 krads
30	Influent sample
31	Effluent sample

Quality assurance, quality control, methods and procedures have been detailed in past reports and test plans.

**#SRL-B1-Ver 1.1-930314
⁶⁰Co Scoping Experiments
Inactivation of Microbial Pollutants**

and

**Test Plan #SRL-B2-Ver 1.0-930314
Full Scale Electron Beam Experiments for
Inactivation of Microbial Pollutants**

Attempts to grow sufficient numbers of bacteria in dechlorinated potable water for full scale tests at the Electron Beam Research Facility (EBRF) have not been successful at pH = 3. Sufficient quantities can, however, be grown at pH = 5. Since experiments conducted as part of our SITE program research have shown approximately four logs of reduction in the carbonate content of our potable water when pH is lowered to 5, scavenging of the hydroxyl radical by carbonate would be minimal at pH = 5. For this reason it is proposed that the above test plans be amended to conduct the proposed experiments at pH = 5 instead of pH = 3.

APPENDIX B

CALIBRATION PROCEDURES

Calibration Procedures for Equipment Used in the Study of Inactivation of Microbial Pollutants

A) Balance: A Mettler PC440 balance is used for weighing all of the chemicals, the agar, and the nutrient broth used in these studies. This balance was calibrated in June of 1992 by a Juno Beach company called Weight Check. It will be calibrated semiannually by the same company.

B) Autoclave: An autoclave from Market Forge (Model STM-EI) is used at a temperature of 250 F and a pressure of 14 psi. The temperature and pressure for each run is recorded in the laboratory notebook. The temperature of the autoclave will be checked with an autoclave thermometer from ERTCO (Model 80135). This thermometer will be calibrated semiannually against an NIST thermometer.

C) Incubator: An incubator from Fisher is used. The temperature is maintained at 37 C and checked twice a day and the temperature is recorded in the laboratory notebook. A thermometer from ERTCO (Model 6391) will be used to check the accuracy of the built-in thermometer of the incubator. Presently it is checked weekly by a thermometer from Fisher (Model 15-000A). The accuracy of the thermometer will be checked semiannually against an NIST thermometer.

D) pH meter: An Orion Research Inc. pH meter is used to measure the pH of the media in which the microbes of interest will be suspended for irradiation. This pH meter is calibrated with two buffers with pH = 4.0 and pH = 7.0 before measuring the pH.

E) Masterflex Precision Dispenser: The Masterflex Precision Dispenser Model 7527-20 is used to dispense 9.0 ml of buffered distilled water into dilution tubes. The dispenser is calibrated to 9.0 ml according to the manufacturer's specifications by checking the accuracy of the volume dispensed with a graduated cylinder.

F) Volumetric Glassware: Serological disposable pipettes from Fisher (calibrated to 1.0 ml) are used to transfer samples into dilution tubes and onto plates. These pipettes comply with ASTM Spec. E714 and are graduated in 1/100 ml divisions.

APPENDIX C

QUALITY ASSURANCE AND CONTROL PLAN

SECTION IIB

**TEST OF ELECTRON-BEAM TECHNOLOGY ON SAVANNAH RIVER
LABORATORY LOW-ACTIVITY AQUEOUS WASTE FOR INACTIVATION
OF BACTERIA**

QA/QC Plan

Submitted By:

Charles N. Kurucz and Thomas D. Waite
University of Miami
Coral Gables, Florida 33124

Savannah River Laboratory

Project Number: D18642EE

Technical Representative: Dr. Jane Bibler
Principal Investigator: Dr. Roger Dougal

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1.0 QUALITY ASSURANCE OBJECTIVES

1.1 QUALITATIVE QA OBJECTIVES

1.1.1 REPRESENTATIVENESS

All bench scale ⁶⁰Cobalt studies will utilize simulant water that contains constituents characteristic of SRL waste that are found to significantly affect bacterial inactivation in the initial scoping experiments (see Test Plan #SRL-B1-Ver 1.0-920-609). The concentrations of significant constituents will closely approximate the weighted average values for actual waste previously provided by SRL.

The experiments that we do at the electron beam will also attempt to utilize simulant water as above with the additional limitation that the quantities of constituents required to obtain target concentrations in 3000 gallon batches may be impractical.

Since timed influent and effluent samples are collected at each irradiation dose to account for transit time, the data generated represent the effect of the actual electron beam process on essentially matched experimental material (i.e., volumes of wastewater).

Also, complete replicates of each experiment require more than one day to execute. Thus variations within day and between days will be present in the sampling process and results will be valid over the naturally occurring variations in water quality and environmental conditions existing at the wastewater facility.

1.1.2 COMPARABILITY

The results of the experiments will be comparable to other studies using ⁶⁰Co gamma sources and/or electron beams of the same voltage (1.5MeV), a weir water delivery system of the same design as at our facility, and performed under similar experimental conditions.

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1.2 DECISION MAKING

The closer the simulant waters used in our studies are to the actual SRL wastewater, the more applicable the results will be to the actual full scale application of electron beam treatment at Savannah River. We fully anticipate that the simulants produced will provide experimental results that can be used to evaluate the applicability of the electron beam process to SRL wastes.

Decisions with respect to the acceptability of data will be implemented by conducting experiments in a step wise manner. If the QA objectives of the experiment are not achieved with respect to the analytical procedures and operational parameters such as dose, the experiment may be replicated as necessary to obtain data suitable for statistical data analysis. Therefore, no decisions will be made if the QA objectives are not achieved, but corrective action will be taken and additional data taken as required. A similar approach will be utilized for bench scale tests at the ^{60}Co source and experiments at the electron beam.

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2.0 SAMPLING PROCEDURES

2.1 BACTERIAL SAMPLING PROCEDURE

Samples will be collected leaving ample air space in the bottle (at least 2.5 cm) to facilitate mixing by shaking, before examination. We will collect samples that are representative of the water being tested, flush or disinfect sample ports, and use aseptic techniques to avoid sample contamination.

Each sampling bottle will be kept closed until it is to be filled. The stopper and cap will be removed as a unit, without contaminating inner surface of stopper or cap and neck of bottle. The container will be filled without rinsing, and the stopper or cap replaced immediately.

a. Water samples from the E-beam: Sampling ports will be opened fully and water let run to waste for a time sufficient to permit clearing the service line. The water flow will then be reduced to permit filling bottle without splashing. The effluent sampling line will be steam cleaned before each experiment. Matched effluent/influent samples will be taken by holding the time between samples equal to the approximate transit time between sampling ports.

b. Size of sample: The volume of sample taken will be sufficient to carry out all tests required.

c. Holding time and temperature: The microbiological examination of a water sample will be started promptly after collection to avoid unpredictable changes. If samples cannot be processed within 1 h after collection, an iced cooler will be used for storage during transport to the laboratory.

All wastewater samples will be held below 10° C, according to standard method 9060B, during a maximum transport time of 6 h. Samples will be refrigerated upon receipt in the laboratory and processed within 2 h. If local conditions necessitate delays in delivery of samples longer than 6 h., field examinations will be considered using laboratory facilities located at the E-beam.

2.2 PREPARATION AND CLEANING OF SAMPLING EQUIPMENT AND CONTAINERS

Prior to use, sample bottles will be rinsed with distilled water, alcohol, and receive a final rinse in distilled water. These are then sterilized in an autoclave at 121° C for 15 minutes.

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3.0 ANALYTICAL PROCEDURES AND CALIBRATION

3.1 FACILITIES AND PERSONNEL

a. Ventilation: Our laboratories are well ventilated and maintained free of dust, drafts, and extreme temperature changes. Central air conditioning is used to reduce contamination, and permit more stable operation of incubators, and decrease moisture problems with media and analytical balances.

b. Laboratory bench areas: We provide a minimum of 2 m linear bench space per analyst and additional areas for preparation and support activities. For stand-up work, the typical bench dimensions are 90 to 97 cm high and 70 to 76 cm deep. For sit-down activities such as microscopy and plate counting, benches are 75 to 80 cm high. Our bench tops are epoxy plastic, an impervious surface that is inert and corrosion-resistant and has a minimum number of seams.

c. Laboratory cleanliness: The laboratory rooms are regularly cleaned and the benches, shelves, floors, and windows are washed. The floors are wet mopped and treated with a disinfectant solution. The bench tops are treated with a disinfectant before and after use. The laboratory is not permitted to become cluttered.

3.2 LABORATORY EQUIPMENT AND INSTRUMENTATION

a. Thermometer/temperature recording instruments: The accuracy of thermometers or recording instruments are checked semiannually against a certified National Institute of Standards and Technology (NIST, formerly National Bureau of Standards, NBS) thermometer or one traceable to NIST and conforming to NIST specifications. These records will be kept in a timely manner in a log book.

b. Balance: The balance is wiped before and after each use with a soft brush made of a material such as camel's hair. The balance pans are wiped after each use and spills are cleaned up immediately with a damp towel. The balances used will be calibrated semi annually. For 2 g or less, we use an analytical balance with a sensitivity less than 1 mg at a 10g load. For larger quantities, we use a pan balance with a sensitivity of 0.1 g at a 150 g load.

c. pH meter: A standardized pH meter with at least two standard buffers (pH 4.0, 7.0, or 10.0) that compensate for temperature before each series of tests is used. A date buffer solution is opened and checked monthly against another pH meter which will be readily available.

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d. Water distillation units: Our water stills produce water of a resistivity of 1.7 megaohm-cm. We use softened water as the source water to reduce frequency of cleaning the still. The still and reservoir are drained and cleaned according to manufacturer's instructions and usage.

e. Media dispensing apparatus: Accuracy of volumes dispensed is checked with a graduated cylinder at start of each volume change and periodically throughout extended runs. If the unit is used more than once per day, then one liter of hot distilled water is pumped through the dispenser to rinse.

f. Autoclave: For items sterilized in the autoclave the temperature, pressure, and time for each run is recorded. A recording thermometer will be used weekly to check the accuracy of the built in temperature control of the autoclave.

g. Safety hood: The filters are checked monthly for plugging or dirt accumulation and are cleaned or replaced as needed. Once per month we expose the plate count agar plates to air flow for 1hr. The plates are incubated at 35°C for 24h and examined for contamination. A properly operating safety cabinet should produce no growth on the plates. We use a pressure monitoring device to measure efficiency of hood performance.

h. Incubator: The temperature is checked and recorded twice daily on the shelf areas. For best results a recording thermometer and alarm system are used. The incubator is placed in an area where temperature is maintained at 16 to 27°C. The incubator temperature is maintained at 37°C and will be recorded twice a day in the logbook. The accuracy of the incubator temperature control will be determined with a thermometer twice a week.

3.3 LABORATORY SUPPLIES

a. Glassware: Before each use, we examine glassware and discard items with chipped edges or etched inner surfaces, with particular attention to screw capped dilution bottles and flasks for chipped edges that could leak and contaminate the work area or create aerosols. Glassware is inspected after washing for excessive water beads and rewashed if necessary.

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b. Utensils and containers for media prep: Utensils and containers of borosilicate glass, stainless steel, aluminum, or other corrosion resistant material are used.

c. Reagents: Only chemicals of ACS or equivalent grade will be used. Chemicals and reagents are dated when received and when first opened for use. We make reagents to volume in volumetric flasks and transfer for storage to good quality inert plastic or borosilicate glass bottles with borosilicate, polyethylene, or other plastic stoppers or caps. Prepared reagents are labeled with name and concentration, date prepared, and initials of preparer, including positive and negative control cultures with each series of cultural or biochemical tests.

d. Dyes and stains: Only dyes certified by the Biological Stain Commission will be used. Bacteriological stains will be checked before use with at least one positive and one negative control culture and results recorded.

e. Membrane filters:

1) Membrane filters and pads for water analyses will meet the following specifications:

- a) Filter diam 47 mm, mean pore diam 0.45 μ m and at least 70% of filter area must be pores.
- b) When filters are floated on reagent water, the water diffuses uniformly through the filters in 15 s with no dry spots on the filters.
- c) Flow rates are at least 55 mL/min/cm² at 25°C and a differential pressure of 93 kPa.
- d) Filters are nontoxic, free of bacterial-growth-inhibiting or stimulating substances, and free of materials that directly or indirectly interfere with bacterial indicator systems in the medium; ink grid is nontoxic. The arithmetic mean of five counts on filters must be at least 90% of the arithmetic mean of the counts on five agar spread plates using the same sample volumes and agar media.

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e) Filters retain the organisms from a 100-mL suspension of Serratia marcescens containing 1000 cells.

f) Water-extractables in filter do not exceed 2.5% after the membrane is boiled in 100 mL reagent water for 20 min, dried, cooled, and brought to constant weight.

g) Absorbent pad has diam 47 mm, thickness 0.8 mm, and is capable of absorbing 2.0 + 0.2 mL Endo broth.

h) Pads release less than 1 mg total acidity calculated as CaCO_3 when titrated to the phenolphthalein end point with 0.02N NaOH.

i) If filter and absorbent pad are not sterile, they will not be degraded by sterilization at 121°C for 10 min. Confirm sterility by absence of growth when a membrane filter is placed on a pad saturated with tryptone glucose extract broth or tryptone glucose extract agar and incubated at 35°C for 24 h.

f. Culture media: We will use the best available materials and techniques in media preparation, storage, and application. We will use commercially prepared media when ever available but note that such media may vary in quality among manufacturers and even from lot to lot from the same manufacturer.

1) Preparation of media: The media will be prepared in containers that are at least twice the volume of the medium being prepared. We will stir the media, particularly agars, while heating, avoiding, scorching or boil-over by using a boiling water bath for small batches of media and by continually attending to larger volumes heated on a hot plate or gas burner, using hot plate-magnetic stirrer combinations. The media will be identified and dated. All the media will be prepared in deionized or distilled water of proven quality. Water volumes and media will be measured with graduates or pipets conforming to NIST and APHA standards, respectively. After preparation and storage, we melt agar media in boiling water or flowing steam. The pH of a portion of each medium will be checked after sterilization and cooling.

2) Sterilization: Media will be exposed to sterilization temperatures for the minimal time as specified below.

Membrane filter	10min @ 121 C
Media and broth	15min "
Dilution water	15min "

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3.4 ANALYTICAL QUALITY CONTROL PROCEDURES

a. General quality control procedures:

1) For membrane filter tests, we will check sterility of media, membrane filters, dilution and rinse water, and glassware and equipment, as a minimum, at the end of each series of samples, using sterile water as the sample.

2) For multiple-tube procedures, we will check sterility of media, dilution water, and glass-ware. To test sterility of media, we subject a representative portion of each batch to incubation at an appropriate temperature for 24 to 48 h and observe for growth. Each batch of dilution water is checked for sterility by adding 20 mL water to 100 mL of a non-selective broth. Alternatively, aseptically we pass 100 mL or more dilution water through a membrane filter and place filter on growth medium suitable for heterotrophic bacteria. We incubate at $35 \pm 0.5^{\circ}\text{C}$ for 24 h and observe for growth. If any contamination is indicated, we reject analytical data from samples tested with these materials and request immediate resampling.

3) For each lot of medium analytical procedures will be checked by testing with known positive and negative control cultures for the organism(s) under test.

4) Duplicate analyses will be performed on 5% of samples and on at least one sample per test run.

b. Measurement of method precision: We will calculate the precision of duplicate analyses for each different type of sample examined, according to the following procedure:

1) Make duplicate analyses on the first 15 positive samples of a specific type, analyzing each set of duplicates by the same analyst, but including all analysts within the laboratory.

2) Calculate the logarithm of each result. If either of a set of duplicate results is zero, we add 1 to both values before calculating the logarithms.

3) Calculate the range (R) for each pair of transformed duplicates as the mean (R_m) of these ranges.

4) Thereafter, analyze 10% of routine samples in duplicate, transforming the duplicates and calculating their range. If the range is greater than $3.27 R_m$, analyst variability is excessive. We then determine if increased imprecision is acceptable; if not, all analytical results are

discarded since the last precision check. We then identify and resolve the analytical problem before making further analyses.

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c. Quality control on membrane filter analyses:

1) Colony verification: For each type of test conducted, colonies will be verified monthly from a known positive sample. If the laboratory has two or more analysts, we will require each to count typical colonies on the same membrane from one positive sample per month. Colonies on the membrane will be verified and the analysts' counts compared to the verified count.

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4.0 DATA REDUCTION, VALIDATION, AND REPORTING

4.1 DATA REDUCTION

4.1.1 INDIVIDUALS RESPONSIBLE

The Quality Assurance Coordinator and Supervisor are responsible for all data reduction. All principal project investigators act in this regard.

4.1.2 SUMMARY OF DATA REDUCTION PROCEDURES

Data reduction involves calculating the population mean and standard deviation of duplicate samples for both influent and effluent samples under a given set of experimental conditions. Both absolute and relative (%) change in populations are then calculated along with dose (krads) for that change.

4.1.3 SUMMARY OF STATISTICAL APPROACH FOR REDUCING DATA, INCLUDING UNITS AND DEFINITIONS OF TERMS

Analysis of variance and regression techniques will be used to analyze the data. The effects of electron dose, water quality and initial populations on each bacteria tested will be analyzed as a factorial experiment using days as blocks. Nonlinear regression analysis will be used to fit curves relating change in population counts to electron dose for each treatment combination found to differ in the analysis of variance.

4.1.4 EXAMPLES OF DATA SHEETS

See Appendix B.

4.1.5 DESCRIPTION OF HOW RESULTS ON BLANKS WILL BE TREATED IN THE CALCULATIONS

a. Counts from unirradiated samples (trip blanks) for the ^{60}Co Bench scale experiments will be used as the denominator in fraction surviving calculations as will unirradiated influent samples for E-Beam experiments.

Also see Sections 2.0 and 3.0.

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4.2 DATA VALIDATION

4.2.1 INDIVIDUALS RESPONSIBLE

The Quality Assurance Coordinator and Supervisor are responsible for all data validation. All principal project investigators act in this regard.

4.2.2 PROCEDURES FOR DETERMINING OUTLIERS AND FLAGGING DATA

Data Identification Checks - all data will be checked to ensure they are properly identified. The three identification fields which must be correct are time, location, and parameter. This information is used to explain why data are not reported for a specific time interval, and it can be the basis for deleting data.

Unusual Event Review - a log will be maintained to record such extrinsic events that can explain unusual data (e.g., power outages, etc.). This information is used to explain why data are not reported for a specific time interval, or it can be the basis for deleting data.

Deterministic Relationship Checks - individual parameters will be routinely checked to ensure that the measured values on an individual parameter do not exceed the corresponding measured control value. This is easily accomplished by data plotting.

Tests for Historical Consistency - this test checks the consistency of the data set with respect to similar data recorded in the past. This is accomplished with the use of Shewhart Control Charts (Section 5.3.5).

4.3 DATA REPORTING

All analysts are responsible for reporting raw data to the Supervisor of Quality Assurance Coordinator for data reduction and validation.

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Figure 4-1. FLOWCHART OF THE DATA HANDLING PROCESS

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5.0 INTERNAL QUALITY CONTROL CHECKS

5.1 SAMPLES

See Section 3.4

5.2 ACCURACY AND PRECISION

See Section 3.4

5.3 CONTROL CHARTS

Dr. Walter A. Shewhart of Bell Telephone Laboratories developed the basic theory for control charts in the 1920's. His book on statistical quality control grew out of this original work. Since then, industrial acceptance of these control chart concepts and other statistical techniques have refined and quantified the quest for quality in manufacturing. Although originally developed for control of production processes when large numbers of articles were being manufactured and inspected on an essentially continuous basis, these same concepts have been readily adopted to laboratory operations where the analyst produces comparatively fewer results on an intermittent basis.

As in the CuSum approach, precision control charts are prepared from duplicate data analyses and accuracy control charts are prepared from known colonies data analyses. Once the control charts are constructed, however, data are plotted as individual values rather than cumulative sums.

Certain constants (factors) are also involved in the preparation of Shewhart Charts, depending upon how the data is grouped, the size of the grouping, and the type of control limit formulation calculation.

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FACTORS FOR COMPUTING CONTROL CHART LINES

Observations in Subgroup (σ)	Factor A_2	Factor D_4
2	1.88	3.27
3	1.02	2.58
4	0.73	2.28
5	0.58	2.12
6	0.48	2.00
7	0.42	1.92
8	0.37	1.86

Inherent in the Shewhart approach is recognition of the basic assumption that variations exist in every method. That is, no procedure is so perfect, so unaffected by its environment, that it will always give exactly the same assay value or product. Where such situations seem to exist, either the device used to measure the process is not sensitive enough or the person making the measurements is not performing properly. For our purposes, the recorded difference between paired samples should never be less than one-half the minimum detectable limit of the parameter under consideration. In the following outlines for preparing precision and accuracy control charts, nitrate data were used to develop the examples. Therefore, the minimum values shown are 0.05 (one-half the detectable limit of 0.1 mg/L as N).

5.3.2.1 PRECISION CONTROL CHARTS

These charts are developed by collecting data for many samples, a minimum of 15 to 20, run in duplicate under assumed controlled conditions. Once these data have been generated, preferable over an extended period of laboratory time, the following steps should be followed to construct the control chart:

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- a) List the range (R) for each set of samples. That is, the absolute value of the difference between each set of samples.

0.10	0.05	0.05	0.05	0.10
0.05	0.05	0.05	0.05	0.30
0.05	0.05	0.05	0.05	0.10
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05
0.05	0.05	0.05	0.05	0.05

- b) Calculate the average range (R_{avg}) by summing the list of R values and dividing by the number of sets of duplicates:

$$R_{avg} = \frac{\Sigma R}{\sigma}$$

$$\frac{2.15}{R_{avg} = 35} = 0.06$$

- c) Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4 R_{avg}$$

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where D_4 is a constant dependent on the number of units in the subgroup. In this case, since two observations are in the subgroup, $D_4 = 3.27$

$$UCL_R = 3.27 R_{avg} = 0.20$$

- d) Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2/3 (D_4 R_{avg} - R_{avg}) + R_{avg}$$

$$UWL_R = 0.15$$

This UWL corresponds to the 95% confidence level.

- e) Now graph R_{avg} , UWL_R and UCL_R in the following manner:

- f) The above precision control chart for nitrates is now complete, and can be used to plot R values on subsequent duplicate samples to determine if the system is in control, out of control (plotted R value beyond the UCL), and/or detect any trends developing within the system.

1. In this example, a trend has developed between duplicate sample sets 4-7. Although the system is not out of control, all variables in the procedure should be checked in an attempt to stop this obvious trend before the UCL is reached.

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5.3.2.2 ACCURACY CONTROL CHARTS

As in the above system, these charts are developed by collecting data for many samples, a minimum of 15 to 20, but on standards under assumed controlled conditions. Again, these data should be generated over an extended period of laboratory time, and be representative of normal operating conditions. The following steps should be followed to construct accuracy control charts:

- List the range (R) and the average (X) of each subgroup of data. Note: In the following example of nitrate data, subgroups of monthly data involving four (4) observations were used:

$$X = \frac{\sum d_{\text{Found} - \text{Actual}}}{n}$$

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Month	Actual	Found	R	X
Sept.	1.1	1.1	0	0
	1.1	1.1		
	1.1	1.1		
	1.1	1.1		
Nov.	1.1	1.1	0.1	-0.025
	1.1	1.1		
	1.2	1.1		
	1.2	1.2		
Oct.	1.0	1.1	0.1	0.025
	1.0	1.0		
	1.0	1.0		
	1.0	1.0		
Dec.	1.0	0.9	0.2	0
	1.0	1.0		
	1.0	1.1		
	1.0	1.0		

- b) Calculate the average range (R_{avg}) by summing the list of R values and dividing by the number of subgroups:

$$R_{\text{avg}} = \frac{\sum R}{\sigma}$$

$$\frac{0.40}{R_{\text{avg}} = 4} = 0.10$$

- c) Calculate the Upper Control Limit (UCL) on the range according to the formula:

$$UCL_R = D_4 R_{\text{avg}}$$

as in the precision control chart. In this case $D_4 = 2.28$

$$UCL_R = 2.28 R_{\text{avg}} = 0.23$$

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- d) Calculate the Upper Warning Limit (UWL) on the range according to the formula:

$$UWL_R = 2/3 (D_4 R_{avg} - R_{avg}) + R_{avg}$$

$$UWL_R = 0.19$$

- e) Now graph R_{avg} , UWL_R , and UCL_R in the following manner:

- f) Turning now to the X values, calculate the UCL_x by the formula:

$$UCL_x = A_2 R_{avg}$$

where A_2 is a constant dependent on the number of units in the subgroup. In this case, since four (4) observations are in the subgroup, $A_2 = 0.73$, therefore,

$$UCL_x = 0.73$$

- g) Calculate the UWL_x by the formula:

$$UWL_x = 2/3 A_2 R_{avg}$$

$$UWL_x = 0.05$$

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Note: Lower Warning Limit (LWL_x) and Lower Control Limit (LCL_x) are simply the negative values of UWL_x and UCL_x respectively.

- h) Now graph the standard Nominal Value (set equal to zero), UWL_x and UCL_x , LWL_x , and LCL_x in the following manner:

Both precision and control charts are constructed for each parameter analyzed utilizing Checkmate QA/QC Software available from Fisher Scientific. Both type of Shewhart control charts are tabulated for inspection during on-site inspections.

Both completeness and method detection limit will be calculated as described in Section 8 of the QA Narrative Statement.

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5.3.3 CALIBRATION STANDARDS

5.3.4 PROFICIENCY TESTING OF ANALYSTS

See Section 3.4.

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APPENDIX A

Glossary of Terms

Biannually: Frequency over the period of one year equivalent to once every six (6) months.

95% Confidence Level: A sample which falls within the upper warning limits determined by the Mean Value $\pm$ 2 Standard Deviation units. Any sample which falls outside this value is discarded and the experiment is repeated.

Control Limits: Used to monitor a measurement system's performance. The upper and lower control limits (UCL, LCL) are determined by the Mean Value $\pm$ 3 Standard Deviation units.

Duplicate Samples: Two or more aliquots obtained from a single sample. These are used to determine precision.

Field/Travel Blanks: Uncontaminated laboratory pure water is transferred to a sample bottle in the field under the same conditions the other field samples are collected. These blanks are used to assure the purity of any preservatives used and to check the technique of the sampler to control vectors of contamination. These blanks are analyzed with the field samples back at the laboratory.

Instrument Calibration: All instruments are calibrated for zero and span prior to analyzing samples.

Measurement Systems Blank: A sample with a concentration of zero for the measurement parameter of the system. This is used for all analyses and standardization procedures with the exception of pH and Temperature.

Proficiency Test Samples: Sample provided by USEPA with unknown concentrations of specific measurement parameters. Passing of these samples is required by HRS as part of the Environmental Water Testing Certification Program.

Quality Control Sample: A sample with a known concentration of a specific analyte that has been verified by analysis using the same measurement system (i.e. USEPA Quality Control Samples).

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Reagent Check: Any reagents with an expired shelf life, discoloration or poor performance are discarded and replaced.

Specialist: A person experienced in specific analytical procedures or methodologies.

Spiked Sample: Any sample altered by the addition of a compound of known concentration for the purpose of obtaining recovery data.

Split Samples: Two identical samples obtained by dividing one sample into two. Each is analyzed by a different operator or laboratory. These are used for intra- and inter- laboratory audits, respectively.

Standards: Analytically prepared reagents of known concentrations. These are used to standardize reagents, calibrate instruments and determine linear regression analysis.

APPENDIX B

Example Data Sheet

The following page describes an example data analysis sheet to be used for both bench scale and pilot scale microbiological studies. Other data sheets will be developed as needed.

**SRL EXPERIMENT
DATA SHEET**

TEST PLAN: _____ EXPERIMENT NAME/NO. _____

SAMPLING DATE: _____ ANALYSIS DATE: _____

MATRIX: _____ RADIATION SOURCE: _____

TECHNICIAN: _____ COMPUTER FILE: _____

BACTERIA	EXPERIMENTAL CONDITION	PLATE COUNT	PLATE COUNT	PLATE COUNT

SECTION III

INTRODUCTION

Chemical analysis of samples did show a significant reduction in the concentrations of benzene and derivatives of benzene following processing through the electron beam facility and they did demonstrate bactericidal properties of the beam as well, for three different kinds of bacteria. On the other hand, the rate of loss of the benzene did not follow the expected first order chemical dynamics with respect to the electron beam dose and the total mass of benzene destroyed by the electron beam appears to be far less than the initial mass instilled in the system. Careful analysis of the results appears to show that a significant fraction of the benzene loss was caused by process(es) other than interaction with the electron beam.

CRITICAL ANALYSIS: FULL SCALE TESTS ON AQUEOUS SOLUTIONS CONTAINING BENZENE

Benzene concentrations were reduced dramatically during the 5-hour test run while irradiating the solution with a 1.5 MeV electron beam. The original influent concentration was 35 mg L⁻¹ and the final effluent concentration was reduced by three-and-a-half orders of magnitude to only 0.008 mg L⁻¹. However, the trajectory of the path from high concentration to low concentration does not seem to follow predictions based on beam-driven chemical dynamics.

According to first order kinetic theory, the ratio $\delta[R]/[R]$ should be proportional to the dose received:

$$\frac{\delta[R]}{[R]} = -k\delta D$$

where $[R]$ is the species concentration, D is the dose, and k is the rate constant. That proportionality is not observed in the experimental data. Table I below shows the influent and effluent concentrations and the dose rate (as taken from Table 12 of the FIU report), and the ratio $\delta[R]/[R]$ computed from these concentration data. The data are listed chronologically. The ratios appear to divide into three groups, as indicated by brackets along the right edge of the table. These groupings appear to correlate more strongly with chronology rather than with dose received.

The first group of 4 measurements, during the first 40 minutes of the test, is characterized by a large benzene loss rate, but the loss rate, though increasing with dose received, is quite lower than linearly proportional to the dose received (see Figure 1) i.e. the rate "constant" k depends inversely on the dose. Exposure to a 500 krad dose removed 88% of the benzene, and exposure to an 800 krad dose removed 97%. These data show a very high rate of destruction of the benzene.

Rate versus Dose

Figure 1. Benzene destruction rate as a function of dose during the first 4 sample intervals. The relationship is sub-linear, indicating a higher efficiency at lower doses. The relatively large zero-dose loss rate is evident.

The second group comprises the set of data points taken during the time interval from 40 minutes to 160 minutes. During that time, the quantity $\delta[R]/[R]$ was constant at a value of 0.31, independent of the dose received including zero dose, thereby indicating that the loss rate depended on some (apparently constant) parameter other than electron beam dose. The third category comprises the time interval from 170 minutes to 325 minutes. During this time interval, the quantity $\delta[R]/[R]$ was 0.80, and was again independent of the dose received - including zero dose. The reason for the change in the rate ratio from 0.3 to 0.8 is not at all apparent.

These data indicate that an effect other than the electron beam accounted for the loss of benzene during the latter stages of these experiments. The significant reductions in benzene concentration that were measured even at zero dose reinforce this argument. Whatever the mechanism by which this anomalous benzene loss occurred, it is important to realize that the loss was specifically associated with passage through the beam delivery apparatus from the point of influent sampling to the point of effluent sampling, otherwise the influent and effluent samples would be indistinguishable. Notable features of the system between those two points include the weir and the catch pan.

Several mechanisms may explain the anomalous benzene loss behavior. The benzene may have reacted with long-lived radicals or with by-products that were created during an earlier exposure, perhaps even being triggered by the fall over the weir. Exposure to air at the weir could lead to air stripping. The step change in the rate ratio could then be attributed to an effect such as the average temperature of the test fluid increasing as the tank truck sat in the sun, a pump warming up, or a ventilation fan in the electron beam room being turned on. Any of these effects could have increased air-stripping losses in the weir system. Temperature probes were used during these experiments to measure dose, so there should be some data available to clarify this.

Perhaps more troubling than the anomalous benzene loss rate is the fact that the total amount of benzene in the system cannot be accounted for if the loss rate is integrated over time. The mass loss rate during each time interval (in mg/min) can be computed from the experimental data by subtracting the effluent concentration from the influent concentration (mg L⁻¹), then multiplying by the flow rate (378 L min⁻¹). The data show that 1.4 kg of benzene

(1.6 L) was initially instilled into 11,400 liters of water, yielding an initial concentration of 123 mg L⁻¹. Integrating the experimental loss rate over the experiment duration yields a final benzene mass of 1.2 kg or a concentration of 108 mg L⁻¹. This is far from the near-zero measurement, and implies a large and uncharacterized loss rate in parts of the system remote from the sampling (electron beam exposure) site. Even using the *initial concentration measurement* of 35 mg L⁻¹ leaves 15 mg L⁻¹ unaccounted for at the conclusion of the test period, and 88 mg L⁻¹ unaccounted for right at the outset.

Effects other than direct electron beam exposure are apparently responsible for a significant amount of the benzene loss. Only the data points in the first group of data appear to show the expected increase of loss rate with increase of beam energy, but even still, a cause and effect relationship between those variables was not actually established. The external losses must be carefully investigated to fully understand the actual chemical dynamics and the real disposition of the "destroyed" benzene.

TABLE I

input concentration [R]	output concentration [R]- $\delta[R]$	dose δD	$\frac{\delta[R]}{[R]}$
35.7	29.5	0	0.17
22.2	5.8	300	0.74
12.1	1.44	500	0.88
6.72	0.17	800	0.97
0.249	0.168	300	0.33
0.232	0.162	500	0.30
0.214	0.145	800	0.32
0.16	0.113	0	0.29
0.151	0.103	300	0.32
0.144	0.046	500	0.68
0.112	0.022	800	0.80
0.098	0.02	300	0.80
0.087	0.014	500	0.84
0.07	0.014	800	0.80
0.055	0.01	0	0.82
0.05	0.01	300	0.80
0.047	0.009	500	0.81
0.04	0.009	800	0.78

At the same time that the benzene concentration behaved curiously, the 4-nitrophenol and the 2-nitrophenol concentrations did follow something close to expectations based on first order rate equations. The data in Tables II and III illustrate this.

TABLE II: 2-Nitrophenol concentration and rate constants.

input concentration [R]	output concentration [R]- $\delta[R]$	dose δD	$\frac{\delta[R]}{[R]}$	$\frac{\delta[R]/[R]}{\delta D}$ (normalized)
0	0	0		
0	1.38	300		
0.74	1.57	500	-1.12	-2.24
0.95	1.13	800	-0.19	-0.24
1.17	1.00	300	0.15	0.48
1.05	0.58	500	0.45	0.90
0.85	0.31	800	0.64	0.79
0.41	0.43	0	-0.05	
0.4	0.25	300	0.38	1.25
0.33	0.12	500	0.64	1.27
0.3	0.06	800	0.80	1.00
0.1	0.06	300	0.40	1.33
0.08	0.06	500	0.25	0.50
0.06	0.06	800	0.00	0.00
0.05	0.05	0	0.00	
0.05	0.05	300	0.00	0.00
0.05	0	500	1.00	2.00
0	0	800		

Table III - 4-Nitrophenol concentration and rate constants.

input concentration [R]	output concentration [R]- $\delta[R]$	dose δD	$\frac{\delta[R]}{[R]}$	$\frac{\delta[R]/[R]}{\delta D}$ (normalized)
0	0	0		
0.31	1.15	300	-2.71	-9.03
0.6	1.33	500	-1.22	-2.43
0.82	0.95	800	-0.16	-0.20
1.01	0.88	300	0.13	0.43
0.95	0.58	500	0.39	0.78
0.8	0.31	800	0.61	0.77
0.41	0.41	0	0.00	
0.4	0.26	300	0.35	1.17
0.35	0.13	500	0.63	1.26
0.29	0.06	800	0.79	0.99
0.1	0	300	1.00	3.33
0	0	500		

Note that the quantities in the last column of Tables II and III should be proportional to the reaction rate constant. During the first few sample intervals, 2 and 4-

nitrophenol were being produced by the action of the beam on the benzene, so the destruction rate constant is largely obscured. However, as the nitrophenol density began to decay, the data show a fairly constant ratio of $\delta[R]/[R]$ to δD until the time when the density becomes small or zero at which point the rate constant is noisy or undefined, respectively. Note also that when the dose was reduced to zero, the nitrophenol concentrations *did not* continue to spontaneously decay like the benzene concentrations did. Thus, the destruction of nitrophenol does appear to be driven almost entirely by the electron beam.

A notable difference between benzene and the nitrophenols is the high water solubility of the nitrophenols. This may explain why the nitrophenol acted predictably while the benzene did not -- the benzene simply evaporated.

The apparent destruction of benzene by processes not immediately related to the beam energy argues in favor of further research into the chemical kinetics that regulate the destruction. Time resolved experiments are necessary to fully characterize and understand these chemical processes. Static storage in two separate tanks, rather than recirculation through one tank, would make the problem much easier to understand, since anything happening inside the input or the output tank could be measured separately.

The data generated during these tests must be considered carefully in order to predict the exposure levels required to reduce benzene concentrations to predetermined levels. The apparent rate constant is approximately 1.1 Mrad per order of magnitude reduction in benzene. This implies a dose requirement of 5 Mrad ($\sim 50 \text{ kJ L}^{-1}$) to effect a reduction from 100 mg L^{-1} to a target of $1 \mu\text{g L}^{-1}$ (drinking water standards allow $5 \mu\text{g L}^{-1}$). The SRL benzene treatment problem involves an aqueous stream with a flow of 20 L min^{-1} . A single-pass system would then require an electron beam power of 1000 kJ/minute or about 17 kW. Operating costs for round-the-clock operation at $\$0.08 / \text{kW-hr}$ amount to about $\$30/\text{day}$ or $\$0.0011$ per liter of water treated.

CRITICAL ANALYSIS: FULL SCALE BACTERICIDAL EXPERIMENTS

Full scale treatment was marginally less lethal to all bacteria than was bench scale testing. Several explanations for that may exist. First, the exposure time in the bench scale test was substantially longer to achieve the same dose - hours compared to minutes. Hence, the bacteria existed in a hostile environment for a greater length of time, leading to a higher mortality rate. Secondly, it is possible that the sampling line at the electron beam was contaminated with bacteria after the test began (while taking the first sample), hence rendering the appearance of a higher survival rate. Some question does remain concerning the precise susceptibility of the bacteria to electron beam irradiation. Data at higher exposures in the full scale tests would be useful to clarify this point. In a practical sense, though, the dose required to eliminate hazardous chemical compounds ($> \text{Mrad}$) greatly exceeds that required to inactivate the bacteria (100 krad) making the question moot.

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