Pacific Northwest Laboratory Annual Report for 1982 to the DOE Office of Energy Research

Part 4 Physical Sciences February 1983

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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J. M. Nielsen and Staff Members
of Pacific Northwest Laboratory

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Pacific Northwest Laboratory
Richland, Washington 99352

PREFACE

This 1982 annual report from Pacific Northwest Laboratory (PNL) to the Department of Energy (DOE) describes research in environment, health, and safety conducted during fiscal year 1982. The report again consists of five parts, each in a separate volume.

The five parts of the report are oriented to particular segments of our program. Parts 1 to 4 report on research performed for the DOE Office of Health and Environmental Research in the Office of Energy Research. Part 5 reports progress on all research performed for the Office of the Assistant Secretary for Environmental Protection, Safety and Emergency Preparedness. Each part consists of project reports authored by scientists from several PNL research departments, reflecting the interdisciplinary nature of the research effort.

The parts of the 1982 Annual Report are:

Part 1: Biomedical Sciences	
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Part 2: Environmental Sciences	
Program Manager - B. E. Vaughan	B. E. Vaughan, Report Coordinator C. M. Novich, Editor
Part 3: Atmospheric Sciences	
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Part 4: Physical Sciences	
Program Manager - J. M. Nielsen	J. M. Nielsen, Report Coordinator J. E. Danko, E. M. Toomey, Editors
Part 5: Environmental and Occupational Protection, Assessment, and Engineering	
Program Managers - S. Marks W. A. Glass	W. J. Bair, Report Coordinator R. W. Baalman, Editor

Activities of the scientists whose work is described in this annual report are broader in scope than the articles indicate. PNL staff have responded to numerous requests from DOE during the year for planning, for service on various task groups, and for special assistance.

Credit for this annual report goes to many scientists who performed the research and wrote the individual project reports, to the program managers who directed

the research and coordinated the technical progress reports, to the editors who edited the individual project reports and assembled the five parts, and to Ray Baalman editor in chief, who directed the total effort.

W. J. Bair, Manager
S. Marks, Associate Manager
Environment, Health and Safety Research
Program

Previous reports in this series:

Annual Report for

1951	W-25021, HW-25709
1952	HW-27814, HW-28636
1953	HW-30437, HW-30464
1954	HW-30306, HW-33128, HW-35905, HW-35917
1955	HW-39558, HW-41315, HW-41500
1956	HW-47500
1957	HW-53500
1958	HW-59500
1959	HW-63824, HW-65500
1960	HW-69500, HW-70050
1961	HW-72500, HW-73337
1962	HW-76000, HW-77609
1963	HW-80500, HW-81746
1964	BNWL-122
1965	BNWL-280; BNWL-235, Vol. 1-4; BNWL-361
1966	BNWL-480, Vol. 1; BNWL-481, Vol. 2, Pt. 1-4
1967	BNWL-714, Vol. 1; BNWL-715, Vol. 2, Pt. 1-4
1968	BNWL-1050, Vol. 1, Pt. 1-2; BNWL-1051, Vol. 2, Pt. 1-3
1969	BNWL-1306, Vol. 1, Pt. 1-2; BNWL-1307, Vol. 2, Pt. 1-3
1970	BNWL-1550, Vol. 1, Pt. 1-2; BNWL-1551, Vol. 2, Pt. 1-2
1971	BNWL-1650, Vol. 1, Pt. 1-2; BNWL-1651, Vol. 2, Pt. 1-2
1972	BNWL-1750, Vol. 1, Pt. 1-2; BNWL-1751, Vol. 2, Pt. 1-2
1973	BNWL-1850, Pt. 1-4
1974	BNWL-1950, Pt. 1-4
1975	BNWL-2000, Pt. 1-4
1976	BNWL-2100, Pt. 1-5
1977	PNL-2500, Pt. 1-5
1978	PNL-2850, Pt. 1-5
1979	PNL-3300, Pt. 1-5
1980	PNL-3700, Pt. 1-5
1981	PNL-4100, Pt. 1-5

FOREWORD

Part 4 of the Pacific Northwest Laboratory Annual Report for 1982 to the Assistant Secretary for Environment, DOE, includes those programs funded under the title "Physical and Technological Programs." The Field Task Program Studies reports in this document are grouped under the subheadings rather than by energy technology as was done last year. Each section is introduced by a divider page which indicates the Field Task Agreement reported in that section. These reports only briefly indicate progress made during 1982. The reader should contact the principal investigators named or examine the publications cited for more details.

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Analytical Studies

• Coal Liquefaction Product Characterization*

Samples of process streams and probable product materials are being obtained from coal liquefaction facilities of varying size (PDU, pilot plant, and, if possible, commercial scale). Materials from several different processes have been obtained, including Solvent Refined Coal (SRC)-I, SRC-II, H-Coal, Exxon Donor Solvent, and Integrated Two-Stage Liquefaction processes. The purpose in obtaining these samples is to subject them to chemical characterization and to biological and ecological testing to evaluate potential health and environmental effects of the coal liquefaction processes. The more basic aspects of this research are funded by the Office of Health and Environmental Research; aspects relating to specific processes or modifications of these processes are funded by the Office of Fossil Energy.

CHEMICAL CHARACTERIZATION OF MATERIALS FROM COAL LIQUEFACTION PROCESSES

W. C. Weimer and B. W. Wilson

Supporting Staff: R. B. Lucke,
C. W. Wright, D. R. Kalkwarf,
E. K. Chess, and D. M. Schoengold

The Pacific Northwest Laboratory (PNL) operated by Battelle Memorial Institute for the Department of Energy prepares, on a periodic basis, status reports that cover specific areas of the coal liquefaction research. The summary of a recently prepared status report dealing with chemical characterization is included at the end of this report. Several additional areas of research activity are described below.

• Chemical Stability of Coal Liquefaction Materials

Several coal liquids have been obtained in large quantities (>25 μ), stored and subsampled throughout long-running biological or ecological testing regimes. The chemical compositions of these materials were determined initially and have been monitored during storage. Furthermore, a study of the stability of these coal liquids under various conditions has been conducted. Components of samples of SRC-II naphthas, middle distillates, heavy distillates, and fuel oil blends and SRC-I light oils, wash solvents, and process solvents stored in the coal liquefaction materials repository at PNL at 4°C in the dark and under a nitrogen atmosphere have been monitored every two years by high resolution gas chromatography. Relative amounts of major components were computed based on the addition of an internal standard. In addition to this biennial monitoring of samples in the repository, studies at 0°C, 20°C, 60°C, and 100°C were carried out using an SRC-II fuel oil blend sample. Any changes in fuel oil components under the conditions of these studies will serve as benchmarks for changes

that may occur over longer periods of time in the repository. Samples of the fuel oil blend stored at 60°C and 100°C were monitored five times during a 32-week period. Samples stored at 0°C and 20°C were monitored annually for the effects of dilution, cover atmosphere, and ultraviolet (UV) irradiation as well as temperature. All data are being analyzed by computer-based pattern recognition techniques.

• Analysis of Highly Polar Components of Coal Liquids by Fast Atom Bombardment Mass Spectrometry

We have recently conducted a preliminary evaluation of fast atom bombardment (FAB) mass spectrometry for the analysis of polar fractions from some SRC-II heavy-end coal liquids. Fast atom bombardment offers several advantages over other mass spectrometry sample ionization modes for the analysis of polar, high molecular weight species. For example, FAB ionizes material directly from the condensed phase without external heating and, hence, does not discriminate against nonvolatile or thermally labile components. Because FAB ionization had been known to yield spectra comprised primarily of molecular ion species, the possibility of applying mass spectrometry/mass spectrometry (MS/MS) techniques to characterize individual components within the complex coal liquid fractions has also been investigated.

The FAB mass spectra of several amino polycyclic aromatic hydrocarbons, tertiary polycyclic aromatic nitrogen heterocycles (PANH), a cyano compound, and hydroxylated secondary and tertiary PANH were characterized by intense molecular ion clusters in which the base peak corresponded to the protonated molecular ion. Biologically active nitrogen subfractions from 750-800°F, 800-850°F, and 850+°F and coal liquid distillates from SRC-II all yielded excellent FAB spectra. Additional experiments indicated the presence of highly alkylated five-ring cata-condensed species in much higher concentrations than previously measured. Collisional activation

*Bullets denote Field Task Proposal/Agreement (FTPA) titles.

analysis of major ions in the FAB mass spectra of the polar coal liquid demonstrated the presence of primary amine groups. The combination of FAB and MS/MS appears to have good potential for determining high molecular weight, nitrogen-containing, multifunctional, bridged and phenylated aromatic compounds. These compounds are, in general, difficult or impossible to determine by high resolution mass spectrometry or gas chromatography. These studies have indicated that there may be more structural heterogeneity in the heavy-end nitrogen fraction of direct liquefaction materials than was previously recognized.

The FAB and MS/MS studies were performed with instrumentation located at the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln. These preliminary experiments were so successful that the VG ZAB-1F mass spectrometer located at PNL is now being upgraded with FAB ionization and a collision cell so that similar work can be conducted in-house.

- Physical/Chemical Degradation of Coal Liquids

Two studies have been initiated to evaluate the effects of physical/chemical/environmental factors on the stability of coal liquids. The first of these involves investigation of whether the mutagenicity and chemical composition of an SRC-II fuel oil blend is altered by exposure to sunlight. This information is needed to assess adequately the health hazards of this material in the event of an outdoor spill. Thin layers of the fuel oil blend were applied to various surfaces and these samples were exposed to light of constant intensity simulating the spectrum and maximum intensity of bright sunshine. The samples were exposed for varying periods while held at a constant temperature in closed quartz containers to avoid thermal reactions and loss of volatile products. After exposure, the samples were fractionated into chemical classes, and the fractions containing the biologically active aromatic amines were tested for mutagenicity by the Ames *Salmonella* assay. In all cases, exposure to sunlight reduced the mutagenicity of a sample irrespective of the composition of its supporting surface; the number of *Salmonella* revertants per microgram was reduced by half following a 9-hour exposure. Further evidence for the photolability of aromatic amines was obtained by exposing toluene solutions of 1-aminoanthracene or 2-aminoanthracene to solar-simulated light. At the same light intensity as used in the experiment described previously, each of these compounds was completely destroyed within 15 minutes. Further experiments are

planned to define more precisely the reductions in mutagenicity of SRC-II products induced by exposure to sunlight and to understand their chemical basis.

The second investigation involves the analysis of a set of samples recently obtained from the SRC-II pilot plant at Ft. Lewis, Washington, which is now being dismantled. The materials collected represent coatings from stairs, railings, walls, floors, and the outside of process equipment. These samples had, therefore, aged in the environment while exposed to oxygen and light for some time. In all cases, these are materials to which workers at a coal liquefaction facility would be exposed. While no toxicity testing has yet been performed on the samples, the results of the preliminary chemical analyses indicate that 4-, 5-, and 6-ring polycyclic aromatic hydrocarbons comprise up to 25% of the total sample and 4-, 5-, and 6-ring amino polycyclic aromatic hydrocarbons comprise up to 3% of the sample. These data suggest the presence of potential mutagenic or carcinogenic agents in some of the samples even after extended environmental exposure.

- Chemical Analysis of Process Materials From Integrated Two-Stage Liquefaction

The study reported here was funded by the Fossil Energy Division of the Department of Energy. This discussion is included in this annual report since it complements the work being performed under OHER direction.

Materials obtained from the Integrated Two-Stage Liquefaction (ITSL) pilot plant in New Brunswick, New Jersey, operated by C. E. Lummus have been analyzed chemically and evaluated for biological activity. The ITSL process represents a significant departure from other direct liquefaction technologies studied thus far. The initial stage is carried out under low severity conditions, and the addition of hydrogen to the process streams takes place in a second stage under selective catalytic conditions, again at fairly low severity. This approach allows a more efficient use of hydrogen and thermal energy. In addition, the low severity results in the formation of fewer polar compounds at low molecular weights; nitrogen is partitioned into higher molecular weight species as compared to the SRC processes, for example.

Recycle process streams in ITSL are composed mainly of 850+°F materials. When these streams are compared to analogous boiling point cuts from the SRC processes, the ITSL streams are substantially lower in mutagenic activity as measured by the Ames assay. Results from chemical analysis show that the

distillate product from the second stage of the ITSL contains a higher proportion of hydroaromatic species than the analogous boiling materials from the SRC processes. Studies utilizing the initiation/promotion assay are not yet sufficiently complete to assess any effect this chemical difference may have on the relative carcinogenic potential of the two types of processes. Since development of the ITSL process is of special interest, studies on materials from the ITSL process will continue into FY 1983.

- Workshop on "Chemical Characterization of Hazardous Substances in Synfuels"

Representatives of the national laboratories involved in synthetic fuel characterization participated in a three-day workshop organized by PNL. Formal presentations were made by 23 of the attendees. The majority of the presentations summarized several years' worth of research at the individual laboratories. The workshop discussion sessions dealt with measurement methodologies, separation and fractionation methodologies, chemical characterization techniques, and quantitative analyses. A proceedings which includes the summary recommendations of the workshop groups, as well as the formal presentations, is being published.

- Chemical Characterization and Genotoxic Potential Relative to Boiling Point for Fractionally Distilled SRC-I Coal Liquids
(Wilson, Pelroy and Mahlum 1982)

SRC-I process solvent (PS) obtained from the Wilsonville, Alabama, pilot plant was distilled into 50°F-range boiling point (bp) cuts at the Air Products research facility in Linwood, Pennsylvania. Chemical analysis of the fractions showed that aliphatic content decreased, while nitrogen-containing polyaromatic compound content increased with increasing bp. The polyaromatic hydrocarbon (PAH) and hydroxylated PAH content also increased with bp. Analysis of amino-PAH (APAH) showed that mutagenic APAHs containing three or more rings were found primarily in fractions boiling above 750°F. Previous studies had identified these as the most mutagenic APAH.

Three microbial tester strains were used to screen for genetically active agents in the SRC-I distillate bp cuts. Reverse mutation with the Ames tester strain TA98 demonstrated that mutagens were concentrated in the bp cuts boiling above 700°F. For this tester strain, most of the genetic activity in these distillates was attributable to chemical fractions enriched in APAH having three or more rings. Mutagenicity data obtained with TA98 were in good agreement with skin carcinogenesis results from the mouse-skin initiation/promotion (in vivo) test system. Forward mutation with TM677 was bimodal as a function of boiling point with most of the genetic activity associated with components boiling between 600° and 700°F. The strongest response in the forward mutation assay did not occur in the most carcinogenically active fractions. Low levels of lambda prophage induction in *Escherichia coli* K12 (strain 8177) were observed for most of the bp cuts and were poorly related to carcinogenesis results.

Results of initiation/promotion experiments used to measure the relative potency of bp cuts as initiators of mouse-skin carcinogenesis again showed that fractions boiling above 750°F were substantially more potent than those boiling below 750°F. The PAHs with boiling points at or above that of the dimethyl benzantracenes were concentrated in the most active bp cut. Compounds reaching their highest concentrations in the highest boiling and most carcinogenically active cut included known carcinogens such as benzo[a]pyrene and dimethyl benzantracene. All biomedical test results indicate that consideration should be given to conducting distillation in an effort to minimize, in the distillate product, the concentrations of those biologically active compounds found in cuts boiling above 700°C (as defined in this study).

REFERENCE

Wilson, B. W., R. A. Pelroy and D. D. Mahlum. 1982. Chemical Characterization and Genotoxic Potential Relative to Boiling Point for Fractionally Distilled SRC-I Coal Liquids. PNL-4277, Pacific Northwest Laboratory, Richland, Washington.

• Oil Shale and Tar Sand Research Materials Preparation and Documentation

Oil shale and tar sand in the United States represent a potential supply of at least 600 billion barrels of crude oil. Continuing commercial interest in developing these reserves has resulted in studies that should help provide assurance to developers that conversion processes are environmentally feasible. A vital part of these environmental studies is the physical and chemical characterization of the effluents that may be generated from the various proposed conversion schemes. Due to the complex nature of the effluents, their characterization has required the development of new procedures for sampling and analysis and for chemical separation. Characterization studies are important and should begin at an early stage of development of a given technology, preferably at the pilot-plant or semiworks stage. In this section, results of the application of these techniques to the characterization of oil shale effluents are presented. Also reported is the progress of a program to provide representative and well-characterized fossil-fuel samples for environmental and health effects studies and for interlaboratory comparison to ensure accuracy of the data.

ORGANIC AND METALLORGANIC PROPERTIES OF OIL SHALE RETORT WATERS

A. P. Toste, K. B. Olsen, C. L. Wilkerson, T. R. Pahl and R. B. Myers

An intensive research effort is currently underway to test the feasibility of using shale oil as a major energy source in the future. Concern about the potential environmental impact of a shale-oil industry has, in turn, prompted research directed at chemically analyzing the potential toxicity of shale oils and the associated retort waters.

Retort waters are coproduced with shale oil during the retorting of oil shale. The quantity and chemical properties of the retort water vary depending upon the retorting technology used; aboveground retorting processes generate much less retort water than shale oil, whereas in-situ processes generate approximately equal amounts of retort water and shale oil. All of the retorting processes designed to date provide for complete recycling of all process waters, with no discharge into the environment. Nevertheless, considering the enormous amounts of retort water that may be produced in a large-scale shale-oil industry, there is considerable concern about the health and environmental impacts associated with the recycling of these waters and any accidental release into the environment.

The primary goal of this study was to analyze the organic and metallorganic properties of oil-shale retort water. Six retort water samples were analyzed: a storage water and a condensate water from the Paraho aboveground retort; a retort water from the Occidental vertical, modified in-situ retort; a retort water from the Geokinetics horizontal, true in-situ retort; a retort water from the Rio Blanco vertical, modified in-situ retort; and a retort water from the

Livermore simulated, modified in-situ retort. The most detailed analysis was of the organics and metals of the Paraho condensate water. The secondary goal of this study was to develop and analyze improved methods of chemically fractionating the complex organic content of retort waters to facilitate their chemical characterization. Steric exclusion chromatography was tested as a means of fractionating metallorganic chelates.

Each retort water (2-10 mL) was loaded on a Sephadex® G-15 column (2.5 cm x 31 cm) and chromatographed at a specific flow rate ranging from 23 to 31 mL/h with milli-Q-purified water. Replicate runs were made with each sample, with and without Blue Dextran as a void volume marker. The column effluent was monitored by ultraviolet (UV) absorbance at 254 nm and collected in 4 mL fractions on an Isco fraction collector. Each column fraction was divided in half: one aliquot was set aside for metals analysis by plasma emission spectroscopy (PES) and instrumental neutron activation (INAA); the other half was methylated prior to gas chromatography (GC) and combined gas chromatography/mass spectrometry (GC/MS) analysis.

Steric exclusion chromatography fractionated the organics in the retort waters into several discrete peaks (Figure 1). Each of the waters studied yielded a distinct chromatographic pattern. Each retort water appears to contain several distinct aggregates with nominal M_ws <1500, based on Sephadex G-15's nominal fractionation range as calibrated against Dextran standards.

Detailed GC and GC/MS analyses of the Sephadex fractions revealed considerable fractionation of the organics (Figure 2).

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FIGURE 1. Steric Exclusion Chromatography of Oil Shale Retort Waters with Sephadex G-15

FIGURE 2. Fractionation of Organics and Metals in Paraho Condensate Retort Water with Sephadex G-15

On the basis of the GC analysis, the first peak fraction (Fraction 27) contained palmitic and stearic acids, along with other carboxylic acids. The second peak fraction (Fraction 36) was easily the most complex, containing a broad spectrum of organics ranging from N-heterocycles to carboxylic acids. Fraction 39, a non-UV-absorbing region, contained carboxylic acids. Finally, the third peak fraction (Fraction 41) contained a moderate variety of polar organics. The metals analysis performed by PES

indicated that metals were fractionated as well (Figure 2). Iron and zinc chromatographed over a wide region, most of which was also associated with organic species. In contrast, most of the manganese chromatographed in very narrow regions associated with organics (Fractions 27 and 29). The metals analysis performed by INAA indicated that arsenic and selenium co-chromatographed in the first UV-absorbing peak (not depicted in Figure 2). The peak fraction (Fraction 27) contained 70% of the total arsenic. A mass recovery calculation for arsenic revealed that the arsenic originally present in the Paraho storage water was quantitatively recovered in the Sephadex fractions.

Steric exclusion chromatography appears to be well-suited for the analysis of retort waters. It provided considerable fractionation of the retort waters' organics and metals. This type of chromatography appears to be amenable to the studies such as the metallorganics study in that it constitutes a rather mild form of chromatography, unlike ion-exchange chromatography, for example. The recovery of arsenic, for example, was quantitative; none was lost due to adsorption on the Sephadex. One might reasonably expect organic-metal chelates to survive the chromatography. Indeed, in our studies to date with the retort waters, certain metals and organic species appear to co-elute, presumably as distinct complexes/chelates or aggregates.

PRODUCT AND EFFLUENT CHARACTERIZATION STUDIES AT RIO BLANCO'S RETORT 1

C. L. Wilkerson, K. B. Olsen, D. S. Sklarew, D. J. Hayes, J. S. Fruchter and C. L. Nelson

Chemical characterization studies of oil-shale pilot plants provide information for assessing the environmental implications of commercial development and for the identification of effluent contaminants which may require or affect control technology. During FY 1982 a Pacific Northwest Laboratory (PNL) field sampling and characterization program was conducted at the Colorado C-a Federal Lease Tract where Rio Blanco Oil Shale Company (RBOSC) was operating a pilot-scale modified in-situ retort. Personnel from PNL and Rio Blanco collected representative samples of product shale oil, retort water, gas condensate, and boiler blowdown. These liquid samples were subsequently returned to PNL for laboratory analysis. On-site gas-phase characterization was conducted to measure several trace constituents in the raw and treated offgas.

The raw offgas was analyzed for sulfur species, nitrogen species, hydrocarbons, mercury, arsenic, and radon. Sulfur compounds

identified using gas chromatography/flame photometry included hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), thiophene, methylthiophene, and sulfur dioxide (SO_2). (The sulfur species are discussed in a separate part of this report.) The total of non- H_2S compounds ranged from 1 to 3% of the total sulfur species measured, which is similar to that found in Rio Blanco Retort 0. Non-ammonia nitrogen species identified by gas chromatography/nitrogen-phosphorus (GC/NP) detector are hydrogen cyanide (HCN), acrylonitrile, acetonitrile, propionitrile, and isobutyronitrile. (The nitrogen species are discussed in a separate part of this report.) A wide range of low molecular weight hydrocarbons has also been observed in the retort offgas. Alkanes, alkenes, and diunsaturated hydrocarbons through decane/decene, including branched components, can be observed by gas chromatography/mass spectrometry (GC/MS) analysis. Aromatic hydrocarbons ranging from benzene through C_4 -alkylated benzenes were also present in the offgas. Levels of vapor mercury in Retort 1 offgas showed a variable behavior with relatively low levels during the first month of the burn and rapid increase (10 to $120 \mu g/m^3$) toward the end of the burn. This behavior has been noted before in laboratory scale retorts. Vapor arsenic levels in untreated Retort 1 offgas were very low during the middle of the burn (July 8-14, 1981) and probably of no process or environmental significance. The observed levels of gas-phase arsenic trioxide and arsine ranged from 2 to 40 and from <0.03 to $0.4 \mu g/m^3$, respectively. These levels correspond to daily releases in the untreated offgas of 1 to 20 grams of As_2O_3 and from <0.02 to 0.2 grams of AsH_3 . No detectable quantities of methylated arsine species were observed.

The sampling for radon in the offgas was conducted toward the end of the burn (October 6-7) with a total of 18 h of data.

The mean concentration was determined to be 28.25 pCi/l with minimum and maximum values of 16.95 and 46.21 pCi/l, respectively. No exact calculations were carried out. However, the concentration of the radon gas in the offgas seemed to be inversely proportional to the flow rate of the offgas.

The flue gas at Rio Blanco Retort 1 was analyzed for SO_2 and polyaromatic hydrocarbons (PAHs). Sampling for SO_2 and PAH was conducted at the cross-over duct from the scrubber to the stack. For SO_2 , a total of 59 h of data from July 11-14, 1981 was collected. The mean and standard deviation was 68.2 ± 26.2 ppm SO_2 . The minimum and maximum values observed for SO_2 were 21 and 135 ppm, respectively. Also during the period two PAH sample runs were made. The sample system consisted of a 1/2 in. stainless-steel probe positioned into the center of the duct, an 8 in. stainless-steel filter holder with glass-fiber/filter (GF/F) material, a one gallon stainless-steel cold trap submerged in an ice-filled bath and two 3 gram Tenax® traps in series at the outlet of the cold trap. Samples were collected for 30 min and returned to the lab for analysis. The results are in Table 1.

Three crude oil shales were analyzed for carbon, hydrogen, nitrogen and sulfur. The average values were 83.9% carbon, 11.68% hydrogen, 1.6% nitrogen and 0.9% sulfur. The sulfur content was significantly lower than that from Retort 0 oil shale (1.9 wt%) whereas the nitrogen content was about the same (1.5 wt%). The decrease in sulfur content in the oil coincided with the decrease in sulfur species in the off-gas stream.

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TABLE 1. Polyaromatic Hydrocarbon (PAH) Component and Total Weights (micrograms).

Component	$\Sigma 1 \mu\text{g}$	$\mu\text{g}/\text{ft}^3(\text{a})$	$\Sigma 2$	$\mu\text{g}/\text{ft}^3(\text{a})$
naphthalene	.06	5.15×10^{-4}	.03	3.46×10^{-4}
acenaphthylene	<.04	—	.03	3.45×10^{-4}
acenaphthene	5.46	4.69×10^{-2}	.09	1.04×10^{-3}
fluorene	<.04	—	<.04	—
9,10-dihydroanthracene	.54	4.64×10^{-3}	.15	1.73×10^{-3}
phenanthrene	.27	2.32×10^{-3}	.25	2.88×10^{-3}
anthracene	.09	7.73×10^{-4}	.07	8.08×10^{-4}
2-methylanthracene	.83	7.13×10^{-3}	.43	4.97×10^{-3}
9-methylanthracene	7.69	6.61×10^{-2}	4.67	5.39×10^{-2}
fluoranthene	1.03	8.85×10^{-3}	.79	9.12×10^{-3}
pyrene	1.65	1.42×10^{-2}	1.40	1.62×10^{-2}
benzo[a]anthracene	.39	3.35×10^{-3}	.23	2.66×10^{-3}
chrysene	1.51	1.30×10^{-2}	.98	1.13×10^{-2}
benzo[k]fluoranthene	1.58	1.36×10^{-2}	.41	4.73×10^{-3}
benzo[b]fluoranthene	.36	3.10×10^{-3}	.04	4.62×10^{-4}
benzo[e]pyrene	7.05	6.06×10^{-2}	.92	1.06×10^{-2}
benzo[a]pyrene	.28	2.41×10^{-3}	.32	3.70×10^{-3}
indeno[1,2,3-cd]pyrene	.15	1.29×10^{-3}	.08	—
dibenzo[a,h]anthracene	<.06	—	<.06	—
benzo[g,h,i]perylene	<.05	—	<.05	—

(a) Stack conditions (600 mm Hg, 71°C).

NITROGEN GAS ANALYSIS AT RIO BLANCO RETORT 1

D. S. Sklarew and D. J. Hayes

Characterization of nonhydrocarbon constituents in potentially valuable retort offgas was continued at Rio Blanco Oil Shale Company's Retort 1 in October 1981 to aid in the assessment of technical, environmental, and health problems posed by these constituents. In this study, five nitrogen species were identified and nine other nitrogen species were tentatively identified. Most of the nitrogen species had not previously been identified in oil-shale retort gases.

Sampling and analysis methods were described in the 1981 PNL Annual Report (Sklarew, Hayes and Olsen 1982). The nitrogen species were analyzed by gas chromatography (GC) using a nitrogen-phosphorus detector (NPD) and two 6-ft glass columns packed with Porapak® QS or Chromosorb® 103.

Five non-ammonia nitrogen species were identified in the retort gas at Rio Blanco by GC: acetonitrile, propionitrile, isobutyronitrile, hydrogen cyanide and acrylonitrile (Table 1). The first three compounds were matched with retention times of their respective standards on two GC columns.

Acrylonitrile and hydrogen cyanide (HCN) were identified on the Porapak QS column. Pyrrole and pyridine were not separated on either column, but a peak corresponding to their mutual retention time was observed on both columns. Standards were not available in the field for other nitriles. However, it seems reasonable to assume the presence of a homologous series of nitriles, especially butenenitrile and pentanenitrile, based on the appearance of the chromatograms. (Additional nitrile standards have since been acquired and we hope to be able to verify these preliminary identifications.) A number of other minor nitrogen species were very tentatively identified by comparison with retention times on the Chromosorb 103 column: pyrrolidine, benzylamine, N-methylaniline, O-toluidine and N,N-diethylaniline. Because most of these peaks are minor components, even coinjection did not give confirmation. Gas chromatography/mass spectrometry (GC/MS) analysis on a Chromosorb 103 column of a grab sample was unable to confirm the presence of any of these nitrogen species in the offgas. All were below detection limits, possibly due to masking of the components by hydrocarbons. Single ion reconstructs were generally not valuable for most of these species due to the overlap of many of their prominent fragment ions with those from the hydrocarbon species. Additional nitrogen compounds

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TABLE 1. Nitrogen Species at Rio Blanco Retort 1 (NPD)

Compound Analyzed	Observed in Retort Gas ^(b)	Method of Identification		
		Gas Chromatography		Gas Chromatography ^(a) Mass Spectrometry
		Porapak® QS	Chromosorb® 103	Chromosorb 103
Hydrogen cyanide	x	x	— ^(c)	
Acetonitrile	x	x	x	
Acrylonitrile	x	x	—	
Propionitrile	x	x	x	
Isobutyronitrile	x	x	x	
Pyrrole or pyridine ^(d)	x	x	x	
?Butenenitrile ^(e)	?			
?Pentanenitrile	?			
Pyrrolidine	?	—	x	
Benzylamine	?	—	x	
N-Methylaniline	?	—	x	
o-Toluidine	?	—	x	
N, N-Diethylaniline	?	—	x	
Methylamine		—	x	
Ethylamine		—	x	
Allylamine		—	x	
sec-Butylamine		—	x	
n-Hexylamine		—	x	
Diallylamine		—	x	
Di-n-propylamine		—	x	
Di-n-butylamine		—	x	
Triethylamine		—	x	
Formamide		x	—	
N, N-Dimethylformamide		x	x	

(a) Gas chromatography/mass spectrometry on a Chromosorb 103 column was unable to confirm nitrogen in the offgas because of hydrocarbon interferences.

(b) Detection limit ~1 ppm.

(c) Standard does not chromatograph on this column.

(d) Standards do not separate on these gas chromatography columns.

(e) Standard not available.

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that were searched for by GC and/or GC/MS, but were below our detection limit, include methylamine, ethylamine, allylamine, sec-butylamine, n-hexylamine, diallylamine, di-n-propylamine, di-n-butylamine, triethylamine, formamide, and N,N-dimethylformamide.

Semi-quantitative results for the nitrogen species are shown in Table 2. Levels shown include the range for most injections during the period indicated. The variation in most of the numbers may be due to sampling problems as well as to changing retort conditions. One compound in which the variation does not appear to be due to injection or dilution is HCN. Peak heights of HCN relative to the other retort gas components appeared to vary considerably during the course of sampling. Excellent separation of hydrocarbons from HCN, as well as reasonably

TABLE 2. Nitrogen Species at Retort 1 (ppm)

	10/17 - 21/81 ^(a)	10/25 - 26/81 ^(b)
Hydrogen cyanide (HCN)	—	6-39
Acetonitrile	n.q. ^(c)	17-58
Acrylonitrile	—	0.5-2
Propionitrile	n.q.	n.q.
Isobutyronitrile	1-7	7-16
Pyrrole or pyridine	1-12	6-45

(a) Chromosorb (Registered trademark of Johns Manville) 103.

(b) Porapak (Registered trademark of Waters Associates, Inc.) QS.

(c) Not quantitated.

good separation from acetonitrile, propionitrile, pyrrole/pyridine and isobutyronitrile, was achieved. To prevent possible quenching of the NPD, acetonitrile was not quantitated on the Chromosorb 103 column because of overlap with and consequent quenching by the acetone solvent. Standard propionitrile was sampled as a vapor above a very small quantity of liquid and therefore could not be quantitated.

REFERENCE

Sklarew, D. S., D. J. Hayes and K. B. Olsen. 1982. "Sulfur and Nitrogen Gas Analysis at Rio Blanco Retorts." In Physical Sciences. Part 4 of Pacific Northwest Laboratory Annual Report for 1981 to the DOE Office of Energy Research, pp. 84-86. PNL 4100 PT 4, Pacific Northwest Laboratory, Richland, Washington.

SULFUR GAS ANALYSIS AT RIO BLANCO RETORT 1

D. S. Sklarew, D. J. Hayes and K. B. Olsen

Sulfur gas analysis was continued at Rio Blanco Retort 1 because of the potential environmental and technical problems created by these components of the retort gas. Seven sulfur species were identified and quantitated at this retort.

All sampling was done at positive pressures through unheated stainless-steel or Teflon® lines. The continual gas flow allowed a state of equilibrium to exist between the gases with the sampling system; therefore, losses were estimated to be minimal. Oil and water condensing in the line were trapped by a glass impinger containing quartz wool. Grab samples were also taken in Teflon-coated steel bombs.

Most analyses were completed on site due to the instability of a number of the retort gas constituents. The grab samples were returned to the laboratory in Richland to confirm field results. Sulfur species were analyzed by gas chromatography (GC) using Porapak® QS and Chromosorb® 107 columns and a Meloy SO₂ analyzer as detector. A Teflon-lined gas sampling valve with a 0.72 m² Teflon sample loop allowed quantitative introduction of the gas samples for sulfur analysis. The GC program rates allowed separation of many of the sulfur species from the more predominant hydrocarbons. This analysis took ~1 h per sample but was

necessary to minimize the pronounced quenching effect of hydrocarbons on the flame photometric detector (FPD).

Four types of standards, depending on availability, were used to identify and quantitate the samples: permeation tubes, gas cylinders, liquid solutions in hexane or acetone, and neat liquids (the last used for qualitative analysis only). Dilutions were necessary to 1) bring the sample gas within the dynamic range of the detectors, and 2) approximately match the sample and standard responses since the FPD response is nonlinear. The dilution apparatus consisted of two rotameters and a glass mixing chamber; or alternatively a vacuum pump was used to evacuate the gas sampling loop and the gas sample was then introduced into the GC at a known reduced pressure to effect a dilution.

Seven sulfur species have been identified in the retort offgas at Rio Blanco by GC or gas chromatography/mass spectrometry (GC/MS): H₂S, COS, CS₂, thiophene and methylthiophene, CH₃SH and SO₂ (Table 1). The first four compounds were matched with retention times of their respective standards on two GC columns. CH₃SH was identified on the Porapak QS column and SO₂ was identified on the Chromosorb 107 column. Gas chromatography-mass spectrometric analysis of a grab sample confirmed the presence of COS, CS₂, thiophene, and methylthiophene. The other species were either masked by other components or were too unstable to survive. Additional sulfur compounds which were searched for by GC and/or GC/MS but were below our detection limits include ethyl mercaptan, isopropyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

The H₂S was not quantitated because of the extremely large dilutions necessary to bring this component within the dynamic range of the FPD. During the initial sampling at Rio Blanco Retort 0, H₂S was determined with a standard Meloy H₂S meter. These measurements agreed well with the numerous on-site measurements made by Rio Blanco Oil Shale Company (RBOSC) personnel and, subsequently, the RBOSC H₂S measurements were used.

Quantitative results for the sulfur species are shown in Table 2. The accuracy of the data, due to the quenching effect of the hydrocarbons, depends on a good separation. Excellent separation of the hydrocarbons from COS and methyl mercaptan, as well as reasonably good separation from CS₂, was achieved.

During operation of Retort 1, a number of what appeared to be good values were

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TABLE 1. Sulfur Species Identified Using Flame Photometric Detector (FPD)

Compound Analyzed	Observed in Retort Gas ^(a)	Method of Identification		
		Gas Chromatography		Gas Chromatography Mass Spectrometry
		Porapak® QS	Chromosorb® 107	Chromosorb 107
Hydrogen sulfide	x	x	x	
Carbonyl sulfide	x	x	x	x
Methyl mercaptan	x	x	— ^(b)	
Carbon disulfide	x	x	x	x
Thiophene	x	x	x	x
Methylthiophene	x			x
Sulfur dioxide	x	—	x	
Ethyl mercaptan		x		
Isopropyl mercaptan			x	
Dimethyl sulfide		x	x	
Dimethyl disulfide		x		

(a) Detection limit ~1-10 ppm.

(b) Standard does not chromatograph on this column.

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TABLE 2. Sulfur Species at Retort 1 (ppm)

	7/14 - 17/81 (Avg.) ^(a)	10/7 - 11/81 (Avg.) ^(a)
COS	100	61 ^(b)
CH ₃ SH	45	85
CS ₂	9	10
SO ₂	10	36
Thiophene	35	27
Methylthiophene	65 ^(c)	23 ^(c)
Total (non-H ₂ S sulfur species)	264	242
H ₂ S	0.9%	1.6%
Non-H ₂ S sulfur species—% of total sulfur species measured	2.8%	1.5%

(a) Average during several days' sampling.

(b) Based on Rio Blanco Oil Shale Company data.

(c) Based on thiophene standard.

obtained during several days' sampling. These values were averaged to obtain the data in Table 2. Some differences in values were seen due to changes in retort conditions. Lower values were generally obtained during routine air injection and higher values were obtained when air injection was reduced. It should also be noted that other retorts at different sites have produced significantly different concentrations of

H₂S and other sulfur species in the retort gas. For example, at Occidental Oil Shale Incorporated's Retort 6, H₂S values ranged from 0.05-0.33% and COS values ranged from 1-40 ppm (Loucks 1979). At Rio Blanco's Retort 0, H₂S values were as high as 3.7% and COS ranged from 85-500 ppm (Sklarew, Hayes and Olsen 1982). The higher concentrations at Rio Blanco may be due to the higher sulfur content of the oil shale at the C-a lease tract (Wilkerson et al. 1982).

REFERENCES

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THE ANALYSIS OF RIO BLANCO 1 SOUR WATERS

K. B. Olsen and R. W. Sanders

Samples of Rio Blanco Retort 1 sour waters were collected at three sampling points. These included one sample from the transfer line to a water storage tank (TK102), six samples from the storage tank (TK102), and four samples of condensate water (D101). The samples were analyzed for trace elements by DC plasma emission spectroscopy as well as for pH, alkalinity, ammonia, total oxygen content (TOC), chemical oxygen demand (COD), and conductivity (Table 1). Comparison of the TK102 samples demonstrated a number of trends: alkalinity, ammonia, and conductivity peaked at sample RB-1-SW-064 and decreased to a minimum at RB-1-SW-122; TOC and COD peaked at the RB-1-SW-122 sample. In all cases, the trace element concentrations were very low with the exception of

potassium, magnesium, calcium, sodium, and silicon. The relative abundance of these latter elements indicates the presence of groundwater, as expected in an in-situ retort. There are considerable differences in alkalinity, ammonia, TOC, conductivity, COD, and magnesium concentration between the transfer line and tank samples collected on July 16, 1981 (RB-1-SW-041 and RB-1-SW-042). These differences may not be significant since the sample taken from the tank was an integrated sample whereas that from the transfer line was an instantaneous sample.

Notable trends observed in the D101 condensate samples were seen in alkalinity, ammonia, TOC, and conductivity which increased through the sample period, maximizing at the RB-1-SW-092 sample. Again, as in the TK102 sample results, there were only very low concentrations of trace elements with the exception of sodium, magnesium, and silicon.

TABLE 1. Chemical Characteristics of Rio Blanco Retort 1 Sour Water (ppm unless noted)(a)

	RB-1-SW-041 7-16-81 TK102	RB-1-SW-042 7-16-81 Line to TK102	RB-1-SW-064 7-29-81 TK102	RB-1-SW-072 8-6-81 TK102	RB-1-SW-085 8-13-81 TK102	RB-1-SW-093 8-24-81 TK102	RB-1-SW-122 10-7-81 TK102	7-17-81 D101 Con- densate	RB-1-SW-063 7-29-81 D101 Con- densate	RB-1-SW-073 8-6-81 D101 Con- densate	RB-1-SW-092 8-24-81 D101 Con- densate
pH	7.50	8.35	8.60	8.65	8.60	8.6	8.8	8.45	8.60	8.65	8.69
Alkalinity (mg/ l as CaCO ₃)	764	4660	7633	6875	6025	4940	3614	2110	2140	7000	9215
Ammonia (mg/l)	227	1410	2340	2140	1640	1670	1210	695	769	2230	3100
TOC (mg/l)	102	405	568	705	725	464	1170	40	42	196	202
Conductivity (mhos/cm)	4000	10400	14000	12700	12200	10200	7500	4500	4400	11900	13600
COD (mg/l)	485	1520	2210	2910	2950	1800	4220	218	237	1070	990
A	0.12	0.03	<0.02	0.08	0.02	0.08	0.10	<0.01	<0.01	<0.01	<0.01
As(b)	N.A.	0.32	0.25	N.A.	0.16	0.17	N.A.	N.A.	0.076	0.24	0.92
B	0.60	0.62	0.65	0.58	0.56	0.55	0.45	0.10	0.10	0.12	0.03
Ca	13	11	6.5	4.3	6.2	5.6	4.7	7.2	2.2	2.2	1.7
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	0.011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.008	<0.005	<0.005	<0.005	<0.005	<0.005	<0.0012	<0.005	<0.005	<0.005	<0.005
Fe	0.16	<0.02	0.33	0.09	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	66	88	78	94	79	74	55	<1	<1	4.2	1.9
Mg	344	164	120	72	68	64	36	50	56	56	18
Mn	0.12	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.06
Mo	0.18	0.20	0.24	0.20	0.18	0.12	0.10	<0.01	0.03	0.03	0.01
Na	760	750	1160	920	1030	650	600	152	175	182	45
Ni	0.09	0.03	0.02	<0.01	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.08	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	N. D.	<0.011	0.026	N.D.	<0.011	0.010	N.D.	N.D.	<0.007	0.030	0.012
Si	12.2	13.7	15.5	13.5	13.8	13.5	13.3	8.4	9.9	10.6	3.7
V	<0.02	<0.02	<0.02	<0.02	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01
Zn	<0.01	<0.06	0.02	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

(a) Trace metals determined by DC plasma emission spectroscopy.

(b) As & Se determined by XRF.

N.A. = not available by XRF; <0.5 by PES.

N.D. = not determined.

FOSSIL FUEL RESEARCH MATERIALS

C. L. Wilkerson, J. S. Fruchter and
D. S. Sklarew

The purpose of the Fossil Fuel Research Materials program is to obtain, store, prepare, and distribute representative samples of new synthetic fuels and associated by-product materials for subsequent Department of Energy (DOE) research studies. Representative samples of feedstocks, synfuels and associated by-product materials are homogenized, chemically characterized, and then used in DOE studies of analytical procedure development, environmental pollution, health effects, and effluent treatment research and development.

A number of samples from oil shale retorts and coal conversion processes that are available in our refrigerated repository were listed in the 1981 PNL Annual Report (Wilkerson and Fruchter 1982). The major new oil-shale research materials added to the repository in FY 1982 were obtained from operations of Occidental Oil Shale, Inc. (OOSI) at the Logan Wash facility in Colorado. Samples of dry oil, offgas condensate oil, heater treater sludge, retort water,

offgas condensate water, and boiler blowdown were obtained from the retorting of Occidental Retorts 7 and 8 (Table 1). Samples of crude shale oil, retort water, gas condensate, and scrubber blowdown were also obtained from the retorting of Rio Blanco Retort 1. Chemical characterization and health effects studies are in progress on these new oil-shale research materials.

In addition, a raw shale core (CE 709) was obtained from Rio Blanco. Elemental characterization of this core was accomplished by X-ray fluorescence (XRF) (Figure 1 and Table 2). All the elements analyzed appeared to be quite variable throughout the core. The sulfur content was of particular interest and was quite variable, ranging from 0.57 to 3.05%.

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TABLE 1. Samples Collected from Occidental Retorts 7 and 8

Sample	Sampling Frequency	Amount/ Sample	Number of Samples		
			Retort 7	Retort 8	Combined
Retort water	Every 2 weeks;	500 ml	18	18	
	Once during burn	20 l	1	1	
Offgas condensate water	Every 2 weeks;	500 ml			18
	Once during burn	20 l			1
Boiler blowdown	Every 2 weeks;	500 ml	18	18	
	Once during burn	20 l	1	1	
Product oil (dry oil)	Every 5000 bbls	500 ml			22
Light oil (offgas condensate oil)	Every 5000 bbls product oil	500 ml			22
Heater treater sludge	Periodically	2 l			8
Product oil composite	Once at end of burn	20 l			1
Light oil tank composite	Once at end of burn	20 l			1

FIGURE 1. Rio Blanco Retort 1: X-ray Fluorescence (XRF) Analysis of Raw Shale Core (Core CE 709)

TABLE 2. Rio Blanco Retort 1: XRF Analyses of Raw Shale Core (Core CE 709).

Std. Values	Al%		Si%		S%		K%		Ca%		Ti%		Mn ppm	
Anvil Points Raw Shale Standard ^(a) (8/24/77)	3.45	0.21	13.9	0.71	0.58	0.03	1.62	0.08	10.0	0.5	0.17	0.01	343	21
466'-488' ^(b)	2.86	0.18	10.3	0.5	1.11	0.06	0.90	0.05	12.6	0.6	0.17	0.01	238	16
492'-493.8'	2.67	0.17	10.2	0.5	0.63	0.04	0.98	0.05	12.9	0.6	0.147	0.008	212	15
562'-564'	4.42	0.26	15.2	0.8	1.16	0.06	2.11	0.11	8.68	0.43	0.18	0.01	314	20
566'-568'	6.29	0.35	19.2	0.9	2.04	0.11	2.75	0.14	4.35	0.22	0.23	0.01	264	17
570'-572'	4.15	0.24	13.5	0.7	1.36	0.07	1.82	0.09	7.25	0.36	0.172	0.0009	285	17
574'-576'	4.62	0.26	16.5	0.8	1.03	0.06	2.45	0.12	7.65	0.38	0.24	0.01	376	23
578'-580'	4.62	0.25	15.5	0.8	1.02	0.06	2.63	0.13	8.62	0.43	0.19	0.01	324	20
582'-584'	3.76	0.22	14.8	0.7	0.89	0.05	2.96	0.15	8.21	0.41	0.19	0.01	279	17
586'-588'	5.01	0.29	18.2	0.9	1.42	0.06	3.27	0.17	5.11	0.31	0.19	0.11	296	19
591'-593'	4.57	0.26	16.1	0.8	0.86	0.05	3.13	0.16	8.17	0.41	0.25	0.01	4.22	25
595'-597'	4.64	0.27	1.17	0.9	1.28	0.07	2.75	0.14	6.67	0.33	0.21	0.01	271	17
604.6'-606'	5.50	0.32	20.7	1.0	1.52	0.08	2.40	0.12	5.06	0.25	0.23	0.01	304	19
613'-615'	4.18	0.24	15.7	0.8	0.86	0.05	3.55	0.18	8.92	0.45	0.24	0.01	407	25
617'-619'	4.50	0.26	16.4	0.8	1.25	0.07	3.97	0.20	7.59	0.38	0.24	0.01	429	26
623.2'-625'	4.48	0.26	16.1	0.8	1.30	0.07	3.24	0.16	7.60	0.38	0.21	0.01	330	20
627'-629'	5.83	0.32	21.3	1.1	1.27	0.07	3.29	0.17	4.31	0.22	0.19	0.01	237	16
631'-633'	5.39	0.30	18.5	0.9	1.20	0.06	3.46	0.17	5.88	0.29	0.26	0.01	279	18
635'-638'	5.90	0.33	19.2	0.9	1.66	0.09	3.32	0.17	5.28	0.26	0.23	0.01	278	18
624'-644'	5.02	0.28	17.4	0.9	2.01	0.11	3.76	0.19	5.57	0.28	0.20	0.01	271	18
646'-648'	4.75	0.27	16.5	0.8	2.12	0.11	3.56	0.18	6.23	0.31	0.21	0.01	303	02
649.5'-652.4'	3.64	0.22	15.4	0.8	1.05	0.06	3.45	0.17	9.15	0.46	0.20	0.01	285	19
661'-663'	4.02	0.24	16.2	0.8	1.05	0.06	4.31	0.22	8.19	0.41	0.19	0.01	302	19
657'-659'	4.34	0.26	15.9	0.81	3.05	0.16	3.91	0.20	4.59	0.23	0.20	0.01	252	18
665'-667'	3.68	0.22	15.0	0.76	1.26	0.07	3.96	0.20	7.61	0.38	0.20	0.01	2.56	18
669'-671'	4.35	0.26	16.0	0.81	2.75	0.14	2.57	0.13	5.77	0.29	0.19	0.01	240	18
673'-675'	5.10	0.29	18.7	0.95	1.81	0.10	2.64	0.13	4.89	0.24	0.21	0.01	245	19
677'-679'	4.93	0.28	18.0	0.91	1.47	0.08	1.98	0.10	6.74	0.34	0.22	0.01	336	24
681'-683'	5.12	0.29	20.4	1.0	1.06	0.06	1.91	0.10	6.16	0.31	0.22	0.01	289	21
685'-687'	4.54	0.26	18.2	0.92	0.89	0.05	1.52	0.08	8.12	0.41	0.20	0.01	305	20
689'-691'														
693'-695'	4.37	0.25	14.6	0.74	0.79	0.04	1.31	0.07	8.83	0.44	0.18	0.01	366	24
697.3'-699'	4.72	0.27	16.6	0.84	0.72	0.04	1.99	0.10	8.32	0.42	0.22	0.01	3.69	25
701'-703'	2.69	0.17	10.5	0.54	0.63	0.04	1.03	0.05	11.99	0.60	0.15	0.01	432	28
705'-707'	3.60	0.22	14.0	0.71	1.13	0.06	1.28	0.06	9.56	0.48	0.15	0.01	346	21
709'-711'	4.14	0.25	15.5	0.79	1.14	0.06	1.53	0.08	8.02	0.40	0.20	0.01	353	22
713'-715'	4.07	0.24	15.7	0.79	1.20	0.06	1.54	0.08	8.54	0.43	0.18	0.01	304	19
717'-719'	4.56	0.27	17.2	0.87	1.32	0.07	1.79	0.09	6.08	0.30	0.18	0.01	261	17
721'-723'	5.01	0.29	17.4	0.88	2.15	0.11	2.35	0.12	5.30	0.27	0.20	0.01	267	18
725'-727'	4.60	0.27	17.3	0.88	1.01	0.06	1.42	0.07	6.98	0.35	0.19	0.01	279	18
729'-731'	5.61	0.32	19.2	1.0	1.90	0.10	1.89	0.10	5.07	0.25	0.23	0.01	298	20
733'-735'	4.22	0.24	16.4	0.83	0.75	0.04	1.37	0.07	8.97	0.45	0.19	0.01	319	21
745'-747'	3.72	0.22	14.9	0.76	1.63	0.09	1.65	0.08	7.56	0.38	0.15	0.01	249	16
749'-751'	4.86	0.28	17.4	0.88	1.05	0.06	1.90	0.10	7.96	0.40	0.23	0.01	327	21

(a) Prepared at PNL.

(b) Depth of core sample.

TABLE 2. (Contd)

Std. Values	Fe%		Ni ppm		Cu ppm		Zn ppm		Se ppm		Pb ppm		As ppm	
Anvil Points														
Raw Shale	2.11	0.11	26.3	2.5	42.5	2.9	68.9	4.0	3.12	0.45	21.2	1.8	43.3	2.5
Standard(a)														
(8/24/77)														
466'-488'(b)	1.62	0.08	27.1	3.5	33.1	2.5	81.6	4.6	1.54	0.43	26.0	2.0	16.1	1.3
492'-493.8'	1.31	0.07	31.1	2.6	22.5	1.9	67.8	3.9	2.28	0.41	19.4	1.7	11.6	1.0
562'-564'	1.91	0.09	30.2	2.5	32.8	2.3	84.3	4.7	2.16	0.41	16.0	1.6	10.7	0.9
566'-568'	2.47	0.12	23.2	2.2	51.2	3.2	120	6	2.03	0.42	35.9	2.5	7.96	0.99
570'-572'	1.67	0.08	24.9	2.2	43.4	2.8	81	4	2.23	0.42	26.8	2.1	14.3	1.2
574'-576'	2.06	0.10	30.3	2.6	32.4	2.4	103	6	0.77		20.7	1.7	10.4	1.0
578'-580'	1.99	0.09	31.7	2.6	35.1	2.5	84	5	0.90	0.41	23.2	1.9	9.9	1.0
582'-584'	1.45	0.07	24.3	2.1	22.3	1.8	72	4	0.74		16.6	1.6	8.9	0.9
586'-588'	1.79	0.09	22.1	2.1	33.8	2.4	97	5	1.51	0.40	23.3	1.9	7.1	0.9
591'-593'	1.90	0.09	24.2	2.4	23.8	2.0	93	5	1.15	0.40	15.2	1.6	8.3	0.9
595'-597'	1.87	0.09	25.2	2.2	33.0	2.3	97	5	1.36	0.39	23.9	1.9	7.1	0.9
604.6'-606'	2.23	0.11	24.7	2.2	30.8	2.3	92.7	5.1	1.14	0.39	23.5	1.9	6.72	0.86
613'-615'	1.97	0.09	28.6	2.5	24.8	2.1	83.4	4.7	0.94	0.41	13.3	1.6	9.17	0.95
617'-619'	2.42	0.12	35.1	2.9	32.8	2.5	109	6	0.84		18.5	1.7	15.5	1.2
623.2'-625'	2.07	0.10	25.8	2.4	29.8	2.3	90.3	5.0	1.55	0.40	18.0	1.7	11.9	1.1
627'-629'	1.95	0.09	26.4	2.3	42.4	2.8	98.6	5.4	1.49	0.39	27.3	2.0	11.7	1.0
631'-633'	2.12	0.11	26.3	2.4	48.3	3.1	111	6	1.75	0.41	32.8	2.3	14.5	1.2
635'-638'	2.37	0.12	24.5	2.4	60.0	3.7	116	6	1.41	0.43	38.7	2.6	9.3	1.1
624'-644'	2.72	0.14	21.7	2.4	37.7	2.6	99	5	0.81		24.4	2.0	6.83	0.94
646'-648'	2.99	0.15	35.0	3.0	36.5	2.7	107	6	1.32	0.42	20.7	1.8	11.1	1.1
649.5'-652.4'	1.78	0.09	25.3	2.3	23.6	2.0	89	5	1.22	0.39	14.3	1.6	10.7	0.9
661'-663'	1.68	0.08	28.8	2.4	26.7	2.1	79	4	1.03	0.39	14.0	1.5	18.4	1.3
657'-659'	2.57	0.13	36.1	3.6	53.3	3.9	106	6	3.28	0.57	34.9	2.7	15.4	1.5
665'-667'	1.58	0.08	23.2	2.3	21.8	2.0	73.3	4.3	1.65	0.45	12.7	1.6	16.3	1.3
669'-671'	2.06	0.10	23.6	2.8	50.2	3.5	92.1	5.4	4.03	0.57	21.8	2.1	16.8	1.5
673'-675'	2.30	0.12	31.7	3.2	59.1	4.0	125.4	7.0	4.31	0.61	37.1	2.8	25.0	1.9
677'-679'	2.87	0.14	29.4	3.3	36.4	3.1	104	6	3.02	0.55	24.6	2.3	15.0	1.5
681'-683'	2.21	0.11	27.6	3.0	42.9	3.2	99.9	5.8	2.21	0.54	19.2	2.1	14.9	1.4
685'-687'	1.97	0.10	21.9	2.4	26.4	2.2	81.9	4.7	1.42	0.44	14.0	1.6	17.0	1.3
689'-691'					28.8	2.6	85.6	5.4	1.81	0.54	15.7	2.0	18.1	1.5
693'-695'	2.03	0.10	29.4	2.9	40.8	3.1	77.9	4.7	2.37	0.54	10.5	1.7	18.4	1.5
697.3'-699'	1.99	0.10	26.8	3.0	37.8	3.0	116	7	1.89	0.53	13.5	1.8	20.9	1.6
701'-703'	1.82	0.09	31.4	3.1	21.2	2.3	63.5	4.0	1.65	0.55	8.5	1.7	37.2	2.3
705'-707'	1.56	0.08	24.4	2.2	22.8	1.9	62.1	3.6	2.02	0.45	9.9	1.5	24.9	1.6
709'-711'	1.87	0.09	26.5	2.4	30.7	2.3	83.0	4.7	2.84	0.44	11.9	1.5	14.2	1.1
713'-715'	1.75	0.09	22.4	2.2	35.4	2.5	86.9	4.9	1.30	0.42	10.2	1.5	12.3	1.0
717'-719'	2.09	0.10	24.6	2.4	52.8	3.4	88.6	5.0	2.69	0.45	18.1	1.8	19.5	1.4
721'-723'	2.23	0.11	30.6	2.7	61.0	2.7	105	6	2.84	0.48	30.7	2.3	45.2	2.6
725'-727'	2.03	0.10	26.8	2.4	37.5	2.6	94.1	5.2	1.42	0.43	15.9	1.7	15.6	1.2
729'-731'	3.08	0.15	40.9	3.3	96.9	5.6	128	7	4.23	0.54	42.6	2.8	37.8	2.3
733'-735'	2.18	0.11	23.2	2.5	16.7	1.8	72.3	4.2	1.02	0.43	11.0	1.5	7.22	0.92
745'-747'	1.37	0.07	30.5	2.4	37.3	2.6	73.6	4.2	2.83	0.44	19.0	1.7	25.9	1.7
749'-751'	2.01	0.10	19.8	2.4	30.8	2.5	95.5	5.4	1.26	0.44	16.6	1.7	14.4	1.2

(a) Prepared at PNL.

(b) Depth of core sample.

Measurement
and
Dosimetry

- **Characterization of Synfuels and Combustion Products**

Characterization of process and effluent streams from synfuel plants requires instruments capable of detecting and measuring high molecular weight compounds, polar compounds, or other generally intractable materials. The purpose of this study has been to investigate the application of supercritical fluid chromatographic techniques to this important problem. In this report, the successful interfacing of a supercritical fluid chromatograph to a mass spectrometer is described. Applications include the analysis of mixtures of polynuclear aromatic hydrocarbons and model high molecular weight polymers.

SUPERCRITICAL FLUID CHROMATOGRAPHY/MASS
SPECTROMETRY

R. D. Smith and H. R. Udseth

The combination of capillary column supercritical fluid chromatography (SFC) with mass spectrometry offers unique advantages. The explosive growth in the application of gas chromatography/mass spectrometry (GC/MS) in the last decade and the range of samples not amenable to GC/MS have spurred the development of high performance liquid chromatography/mass spectrometry (HPLC/MS). However, interfacing HPLC to mass spectrometry is a difficult task because of the fundamental incompatibilities in required liquid flow rates and solvent evaporation or removal. The range of compounds which may be separated with SFC is quite similar to HPLC. Both techniques allow the separation of materials which are thermally labile and of much higher molecular weight than is possible using GC. Supercritical fluid chromatography has the added capability of pressure programming, providing precise control of the solvating power of the mobile phase. The much higher volatility of most SFC mobile phases provides a significant advantage in the design of the SFC/MS interface. The use of wall-coated open tubular capillary columns provides mobile phase flow

rates compatible with chemical ionization mass spectrometry. Other advantages accrue from the high chromatographic efficiency possible with capillary columns due to the low pressure drop across the column and the more uniform density of the mobile phase.

The potential advantages of SFC/MS are being explored using newly developed instrumentation. Figure 1 gives an overall schematic of the SFC/MS instrument constructed at Pacific Northwest Laboratory (PNL). The instrument incorporates a high-pressure programmable syringe pump, a constant temperature oven, a 0.2 μ l injector, capillary column SFC, direct fluid injection (DFI) interface, and a tandem quadrupole mass spectrometer equipped with a dual chemical ionization-electron impact ion source.

Fused silica capillary columns, with 100- or 200- μm I.D. and lengths of 10 to 30 m, were used in our initial studies. Capillary columns were prepared by immobilizing the stationary phase through peroxide cross-linking of SE-52 and SE-54. Our work to date has utilized isobutane, *n*-pentane, and carbon dioxide as mobile phases. The principal design considerations for the DFI probe involved obtaining constant temperature conditions, proper column restriction to obtain optimum flow rates, and efficient transfer

FIGURE 1. Schematic Illustration of the SFC/MS Instrumentation

of nonvolatile compounds to the ionization region. The fused silica capillary column is connected to the DFI probe tip by a zero dead volume connection, and a platinum-iridium tubing extends through the last 3 cm of the interface to the flow restrictor which determines the phase flow rate. The DFI probes have been designed to couple with the direct probe inlet of a "simultaneous" chemical ionization-electron impact (CI-EI) ion source. A second CI source inlet provides additional chemical ionization reagent gas (usually the SFC mobile phase). A servo-valve and pressure controller are used to regulate gas flow. Thus, a constant CI source pressure is maintained during SFC pressure programming.

The SFC/MS instrumentation developed at PNL has been successfully applied to a variety of problems (Smith, Fjeldsted and Felix 1982; Smith and Udseth 1982). Our experience to date indicates that any material soluble in the supercritical fluid phase is efficiently transferred to the gas phase. Thus, it appears that CI spectra can be obtained for any compound soluble in a supercritical field.

The capillary SFC/MS interface avoids problems related to solvent evaporation by maintaining supercritical (dense gas) conditions up to the DFI restrictor. Additional advantages result from the much higher volatility of typical mobile phases compared to HPLC, where typical conditions result in extensive cluster formation and persistence of a jet of frozen liquid extending 2 to 5 cm into the vacuum region. In the DFI interface, the *n*-pentane jet disappears at less than 0.5 cm for flows as large as 100 μ l/min. Typical flows show no visible jet. A result of the mobile phase volatility is that the mass spectra show no evidence of ion clusters.

Figure 2 illustrates the selected ion monitoring response obtained for a series of pyrene injections ranging from 20 pg to 20 ng with solvent (hexane) blanks for a flow rate of about 17 cm/s (~30 μ l liquid/min). The mass spectra show a dominant $(M+1)^+$ ion at m/z 203 to be the base peak and no other ions amounting to more than 10% of m/z 203. The signal-to-noise ratio for the $(M+1)^+$ ion is greater than 10 for the 20 pg injection, suggesting detection limits of about 1 pg using selected ion monitoring and 100 pg while scanning. (The lack of linear response at higher concentrations results from the increased dead time for pulse counting at rates exceeding $\sim 5 \times 10^5$ counts/s.)

Figure 3 illustrates the application of the capillary SFC/MS to a mixture of five polycyclic aromatic hydrocarbon compounds in

FIGURE 2. Selected Ion Monitoring (SIM) Response for m/z 203 for a Series of Pyrene Injections

FIGURE 3. SFC/MS Total Ion Chromatogram for a Separation of Polycyclic Aromatic Hydrocarbon Mixtures

methylene chloride. The separation used a 0.2-mm x 20-m column and *n*-pentane as the mobile phase. The SFC pressure program used 15 min at 20 atm followed by a pressure increase of 0.8 atm/min to 40 atm. The injected moisture contained a nominal 40 ng of naphthalene, anthracene, pyrene, benzo[a]pyrene and coronene.

The application of the SFC/MS instrument to nonvolatile high molecular weight compounds is illustrated in Figure 4. This figure gives the reconstructed ion chromatogram for a separation of a polystyrene sample having a nominal molecular weight of 800 using similar conditions. The chromatogram shows the first twelve styrene oligomers to be

FIGURE 4. SFC/MS Total Ion Chromatogram of an 800 Average Molecular Weight Polystyrene Sample

resolved. The molecular weight of the individual oligomers is $104n + 58$. The mass spectra show $(M+1)^+$ ions and distinctive fragment ions for each oligomer, clearly proving the separation and demonstrating that the mass spectra are obtained without detectable decomposition of the individual oligomers. Additionally, the largest peak areas are obtained for the $n = 7$ and $n = 8$ oligomers as would be expected from the

known average molecular weight. These results demonstrate the efficient transfer of compounds (i.e., the larger oligomers) expected to be nonvolatile for the ion source temperature of 210°C .

The development of a reliable SFC/MS interface can be expected to result in the increased application of SFC. This work has demonstrated that the mass spectrometer is a nearly ideal SFC detector, providing comparable or greater sensitivity than alternative methods. The application of the supercritical fluid-mass spectrometer interface has been shown elsewhere to be an effective device for both the direct analysis of supercritical fluid extraction products and as an alternative gentle direct inlet technique for nonvolatile materials.

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• Trace Analysis by Laser Excitation

Lasers, because of their selective and high power emission characteristics, appear promising candidates for sophisticated applications to analytical chemistry. Pacific Northwest Laboratory is actively involved in the development of laser-based systems that are optimized for the analysis of low levels of either inorganic or organic components in environmentally accessible matrices. During the past year major developments have been made in techniques for heavy element detection in water and biologically derived fluids.

LASER EXCITATION AND KINETIC PHOSPHORIMETRY: MEASUREMENT OF URANIUM IN SOLUTION AT THE PARTS-PER-TRILLION LEVEL WITH TRUE INSTRUMENTAL CORRECTION FOR QUENCHING EFFECTS

B. A. Bushaw

Laser-induced phosphorescence with time-resolved photon counting detection has been used to measure uranium, as uranyl phosphate, in aqueous solution at room temperature. Demonstrated detection limits are below 10 parts per trillion. Multichannel scaler (MCS) photon counting is used for the rejection of laser and raman scattering, discrimination against prompt fluorescing species such as organics, and to provide a simultaneous determination of the uranyl emission life time. The life time is then used as a direct (photophysically correct) instrumental correction for matrix quenching and temperature effects. The MCS counting mode also allows rapid measurements [a few seconds at the parts-per-billion (ppb) level, 5 min for parts-per-trillion]. The method has been used for: 1) evaluating uranium contamination in ultrapure solvents and trace analytical procedures in the low part-per-trillion range; 2) directly measuring urine samples at the 10 ppb level without chemical pretreatment or separation; 3) direct measurements on drinking and groundwaters at the sub-ppb level; and 4) using oxidative digestion as the only preparation, both urine and brine waters have been measured at the sub-ppb level.

At these demonstrated detection capabilities, the method is currently being applied to the evaluation of groundwater samples in waste management monitoring and determination of background uranium levels in salt dome structures being considered for waste storage. Since the technique has greater sensitivity, better accuracy, and simpler preparative chemistry than previously available methods, it is expected to have widespread applications in environmental monitoring, geological surveying, and bioassay measurements.

Figure 1 shows a schematic diagram of the instrument. The excitation source is a broad band dye laser pumped by a nitrogen

FIGURE 1. Instrumentation for Laser Excitation Kinetic Phosphorimetry Determination of Uranium.

laser. It is operated at 425 nm with a bandwidth of ca. 10 nm. At a repetition rate of 20 Hz, the peak power is about 50 kW with a 5 nsec pulse duration. The induced emissions are observed at right angles with a dry ice cooled photomultiplier. The only optics used for detection are an f1.0 collection lens and a 520 nm (10 nm bandwidth interference filter). The photomultiplier is used in a photon counting mode with the anode signal processed by fast preamplifier and a discriminator. The scaler output of the discriminator is then used for the actual counting. Photon counting in a time-resolved mode is accomplished with an MCS using a 10 microsecond per channel dwell. The MCS sweep is repetitively triggered by the firing of the laser and a summation of the number of counts in each channel is made for a user specified number of laser shots (typically 600-6000). Figure 2 shows a typical time-resolved emission spectrum obtained with the system. At the end of the MCS data acquisition, the spectra are transferred to a minicomputer for storage and later data analysis.

FIGURE 2. Time-Resolved Emission Spectrum from 0.363 ppb Uranium Standard Solutions. Dwell per channel is 10 microseconds.

The basis for life-time correction of matrix quenching (historically the "boogie man" of uranium phosphorescence analysis) is derived directly from the photokinetics of the emitting state. If a given population of uranyl phosphate is placed in the emitting excited state as a delta function in time, then its evolution may be described by the simple first order differential equation:

$$d[U^*]dt = (k_p + k_q) [U^*]$$

which may be integrated and linearized to the form:

$$\ln[U^*]_t = (k_p + k_q)t$$

$$\ln[U^*]_t = \ln[U^*]_0$$

Thus, plotting the natural logarithm of the emission intensity as a function of time (see Figure 2) yields an intercept of $\ln[U^*]_0$ a direct measurement of the initially created excited state population, independent of matrix quenching effects.

The precision and accuracy of such measurements can be seen in Figure 3, which is a plot of measured concentration versus spike addition concentration for a series of urine samples which were pretreated by HNO_3 and $HClO_4$ digestion. The correlation coefficient of 0.9995 reflects the precision of the measurements. The values determined for

FIGURE 3. Calibration Curve for Analysis of Uranium in Urine

the two independent zero spike addition samples (0.64 and 0.80 ppb) are in good agreement with the standard additions intercept value of 0.57 ppb and may be taken as the actual uranium concentration in the urine matrix.

It is expected that both detection limits and measurement time may easily be improved by a factor of 10 with some changes in the optical system. Measurement time and/or counting statistics may be improved by using a higher repetition rate laser and more efficient collection optics. The detection limits which have been demonstrated thus far are limited by contamination of the reagent grade phosphoric acid used, which contains about 2 ppb uranium. If the 5% solution were made up from ultrex grade phosphorus pentoxide, the background would be reduced by a factor of 15, down to that which arises from emissions from the far UV quartz cell material.

In addition to the rather remarkable measurement capabilities, the instrument is simple and reliable. The system, including the dye laser, dye cell, one mirror and a lens for focusing the pump beam, and the optical train, is inherently simple. Since the electronics are all of the standard nuclear counting variety, the instrument should provide a portable, inexpensive solution to present field and laboratory problems in low-level uranium analyses.

● Instrumentation and Chemical Procedures Development

During the past year, efforts in this program have been concentrated on developing a procedure to measure small amounts of ^{99}Tc by beta counting.

SIMPLIFIED METHOD TO ANALYZE FOR TECHNETIUM-99

C. W. Thomas

Technetium-99 is of importance in the aged waste from the nuclear fuel cycle. It is both an activation product formed from the decay of ^{99}Mo as well as being a fission product. In nuclear waste it is a prominent radionuclide after 100 years of radioactive decay have occurred.

Because of TcO_4^- anion stability, ^{99}Tc migrates readily through soil columns. The simplified procedure developed for ^{99}Tc is based on three chemical characteristics: 1) the extreme solubility of the stable TcO_4^- anion in both acids and bases, 2) the behavior of technetium with rhenium carrier present, and 3) the ease with which technetium electroplates.

Technetium electroplates readily in both acidic and basic solution. Electroplating is not inhibited by copious amounts of alkaline earths or alkaline metal salts.

The simplified radiochemical procedure consists of adding rhenium carrier to the sample, acidifying the sample and scavenging repeatedly by forming iron hydroxide using NaOH and then NH_4OH . The resultant basic solution is evaporated, filtered and the technetium electroplated from an ammonium perchlorate media. Technetium-95 is used to determine radiochemical yield, and then the ^{99}Tc beta is counted through an aluminum absorber to reduce the interference from the ^{95}Tc . Radiochemical yields vary from 40-90%. Several samples can be analyzed in a few hours.

Physical
Processes

● **RADIATION PHYSICS**

A fundamental knowledge of the mechanisms by which radiation interacts with matter is essential for understanding dose-response relationships in terms of quantifiable chemical and physical processes. The Radiation Physics Program is directed toward investigation of the fundamental processes of energy deposition by fast charged particles and the subsequent transport and degradation of that energy as it leads to the formation of chemically active molecular species. The initial deposition of energy is studied through the measurements of total and differential cross sections for production of ions and electrons in collisions of fast charged particles with atomic and molecular targets. These data, when coupled with theoretical calculations, provide insight into the mechanisms of energy deposition in biologically significant matter. They also provide the necessary data base for energy transport studies. Our effort in energy transport and degradation combines the use of Monte Carlo calculations and theoretical investigation of condensed-phase chemical kinetics. Monte Carlo calculations provide detailed information on the initial structure of the particle track, and the theoretical investigation of energy transport provides the link between initial energy deposition and the final observation of chemically active molecular species. Our integrated program of experimental and theoretical investigation results in a unified approach to understanding the mechanisms by which chemically active species are formed as a result of exposure to a radiation field.

This interdisciplinary program in the study of energy deposition, degradation, and transport maintains an active collaboration with scientists at numerous universities and national laboratories. During the past year we have benefited by a close working relationship with research groups, or individuals, at Argonne National Laboratory, GSF-Institut für Strahlenschutz (Neuherberg), Kansas State University, and the University of Nebraska, and by the numerous contacts made at meetings and workshops.

Initial Interaction Process

Our study of the initial interaction processes in the absorption of energy from a radiation field by biologically significant material has concentrated on the measurement and interpretation of total and differential cross sections for the production of electrons and ions in collisions of fast charged particles with atomic and molecular targets. Of particular interest is the determination of cross section systematics and interaction mechanisms which will enable extrapolation of experimental results into regions where experiments are either impractical or unfeasible. A thorough understanding of these processes is particularly important in assessing the reliability of track structure calculations of energy deposition in condensed media based on interaction cross sections obtained from collisions with free atoms and molecules. During the past year, we have continued measurements of total cross sections for ion and electron production resulting from interactions of fast atomic and molecular ions with atomic and molecular targets. This project, in which we collaborate with Prof. M. E. Rudd (University of Nebraska), supplies data needed for our track structure calculations and for more accurate tests of our differential cross sections. Measurements were also initiated to provide information on the degree of multiple ionization which occurs in ionizing collisions. Auger electron spectral measurements and theoretical calculations of inner shell ionization cross sections were conducted to enable a more comprehensive understanding of the mechanisms for production of multiply charged ions. Interpretation of collision cross sections in terms of current theory has concentrated on application of Bethe-Born theory to singly differential cross sections measured for ionization of helium, neon, and argon by protons. This work is particularly important in devising means of extrapolating and interpolating cross sections into regions where data do not exist.

DOUBLY DIFFERENTIAL CROSS SECTIONS FOR PROTON IMPACT ON H_2O AND CH_4

R. D. DuBois, F. M. Cummings,* W. E. Wilson and L. H. Toburen

The spatial distribution of primary energy deposition events along a charged particle track has important consequences in the subsequent chemical and biological processes. Calculations of these distributions, using Monte Carlo techniques, require detailed source information on the energy and angular distributions of secondary electrons.

Doubly differential cross sections (DDCS) for electron emission by proton impact have been extensively studied by our group over the past decade. Of particular biological interest is information about high energy proton impact on water. Our previous work (Toburen and Wilson 1977) was limited to proton energies below 1.5 MeV. We are currently extending these measurements to higher proton energies. Both H_2O and its isoelectronic counterpart, CH_4 , are being studied. These data will complement and supplement existing data and provide Monte

Carlo source terms. During the past year, data have been accumulated at 3 and 3.67 MeV for both H_2O and CH_4 targets. These measurements continue to be plagued by high background contributions from scattered electrons. Methods to suppress this background are being studied and additional measurements will be initiated soon.

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Toburen, L. H. and W. E. Wilson. 1977. "Energy and Angular Distributions of Electrons Ejected from Water Vapor by 0.3-1.5 MeV Protons." *J. Chem. Phys.* 66:5202-5213.

CONSTRUCTION OF A NEW DOUBLY DIFFERENTIAL CROSS SECTION APPARATUS

R. D. DuBois

Traditionally the emphasis in this laboratory has been on measurements of doubly differential cross sections (DDCS) for electron emission from gaseous targets by charged particle impact. Such measurements provide sensitive detailed information about collision processes and severely test theoretical calculations. Due to the complexity of the ionization process, as well as the experimental limitations, our past experimental work has concentrated on DDCS measurements for incident bare projectiles, namely protons and alpha particles. Experimental

* Mr. Cummings is a staff member in the Dosimetry Technology Section, Radiological Sciences Department at Pacific Northwest Laboratory and is participating in the masters program through the University of Washington, Joint Center for Graduate Study.

results from these studies have been found to agree moderately well with Born calculations.

In a limited number of studies, structured projectiles such as He^+ , C^+ , etc., have been used; but for these projectiles the theoretical interpretation is made more difficult because electrons can be ejected from the projectile as well as from the target. A new experimental apparatus (Figure 1) is being constructed to provide the additional versatility needed to gain information about this type of process. The apparatus, which will be completely under computer control, is designed to measure DDCS over a broader angular range than is presently accessible and design considerations allow target and projectile ionizations to be separated through coincidence techniques. Electron emission from specific electronic shells of the target atom or molecule, which can be measured by coincidence methods, is also being considered, as well as electron emission from solid targets. Such studies would greatly aid in our theoretical understanding of the collision process. Construction of the apparatus is nearly complete. Initial installation, debugging, and testing will commence in the near future.

FIGURE 1. Doubly Differential Cross Section (DDCS) Apparatus Showing Rotatable Spectrometer, Collimators, and Alignment Tool Showing Interaction Center

ALIGNMENT DUE TO ELECTRON CAPTURE

R. D. DuBois and C. L. Cocke*

Detailed information about collision processes can be obtained by studying the angular distributions of Auger electrons produced during the collision. Under certain circumstances (Mehlhorn 1968), noniso-

tropic angular distributions of Auger electrons can be directly related to the nonstatistical population of magnetic sub-states (i.e., alignment).

A detailed experimental study of collision-induced alignment in H^+ -Mg collisions (Rødbro, DuBois and Schmidt 1978) was found to agree only qualitatively with theory (Berezhko and Kabachnik 1977). More recently, calculations (Berezhko, Kabachnik and Sisov 1980) have attributed the observed discrepancies to Auger emission following electron capture by the proton that may occur in addition to direct coulomb ionization. In the calculations of Berezhko, Kabachnik and Sisov the alignment due to direct 2p ionization and 2p electron capture by the projectile, as well as accurate total 2p ionization and capture cross sections, must be known in order to compare with the experimental data that are a weighted average of the individual alignments.

As a first step in evaluating the theoretical work, we have collaborated with Prof. C. L. Cocke of Kansas State University to measure the ratio of 2p electron capture to direct 2p ionization for the H^+ -Mg system. The results shown in Figure 1 were presented at the International Conference on X-Ray and Atomic Inner-Shell Physics in August 1982 (DuBois et al. 1982).

FIGURE 1. Ratio of 2p Capture/Direct Ionization Cross Sections for Proton Impact on Atomic Mg

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* Work performed in collaboration with Professor C. L. Cocke at Kansas State University.

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TOTAL ION AND ELECTRON YIELDS

R. D. DuBois and M. E. Rudd*

Absolute doubly differential cross sections (DDCS) provide sensitive detailed information about ion-atom collision processes. In principle, such data, differential in angle and energy of electron emission, can be integrated to provide total ionization cross sections. Difficulties in measuring DDCS for low energy secondary electrons, however, as well as other inherent uncertainties in this type of measurement, limit the accuracy of total ionization cross sections obtained in this manner.

Thus, direct measurements of total ion and electron yields were initiated in 1981 in collaboration with Professor M. E. Rudd (University of Nebraska). The emphasis of these studies is on accurate (better than 10%) absolute cross sections for proton-gas collisions and on measurements that extend over a wide energy range. The energy range covered in this work is from 5-4000 keV. These cross sections, which are important in track structure calculation normalization procedures, can also help us assess the accuracy of our existing DDCS data--particularly at low secondary electron energies.

Total ion and electron yields are obtained in the following manner. An electric field between condenser plates is used to extract ions and electrons produced during the H^+ -gas collision. Measurement of these currents, normalized to target gas density and proton beam current, allow total ion and

electron production cross sections (σ_i , σ_e) to be determined. For unstructured projectiles such as H^+ , the total electron yield (σ_e) corresponds to the total ionization cross section for the target, whereas the difference between the ion and electron yields ($\sigma_i - \sigma_e$) provides the electron capture cross section. In the case of structured projectiles (e.g., He^+) the electron yield results from ionization of the target and electrons stripped from the projectile, whereas the ion yield is from ionization of the target only.

To date, data have been accumulated for proton impact on eleven gases which include both atoms and simple molecules. Preliminary data were presented during the year (DuBois et al. 1982). The major emphasis in this project during the past year has been on error analysis and data reduction.

In order to average out small experimental errors and to concisely present the vast amount of data accumulated, we are developing a program to least-squares fit the data with an empirical equation of the form

$$\sigma_e = 4\pi a_0^2 I_H^2 A \sum_i \frac{N_i}{I_i^2} \frac{(T/I_i)^B}{C + (T/I_i)^{B+1}} \ln(1 + D T/I_i)$$

where I_H = ionization potential of atomic hydrogen

N_i = number of electrons in target shell i

I_i = ionization potential of target shell i

T = reduced proton impact energy

A, B, C, D = fitting parameters.

A preliminary fit to the H^+ -He data is shown in Figure 1 for ionization of helium by protons. Other targets are presently being

FIGURE 1. Ionization Cross Section for Proton Impact on He. The dashed empirical curve is fitted to the data as described in the text.

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fitted in a similar manner and it is anticipated that the same technique will be applied to fitting σ_i .

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PARTIAL IONIZATION CROSS SECTIONS FOR PROTON IMPACT

R. D. DuBois

In our total yield experiments, yields are measured with no energy or charge resolution. Therefore, the measured cross sections σ_i include multiple as well as single ionization of the target. For example, we measure the sum of the following reactions:

Since neither our total nor differential cross section measurements distinguish between these processes, comparison with theoretical single ionization cross section calculations is difficult.

To study the production of multiply charged target species we have added a time-of-flight (TOF) charge state analyzer to the condenser plate system used in the total yields measurement. The analyzer (Figure 1)

FIGURE 1. Parallel Plate Condenser System and Time-of-Flight Ion Charge State Analyzer

accelerates slow target ions, charge state q , to an energy qV and pulses them into a drift tube. After exiting the tube, they are detected and their flight time is recorded. The flight time, proportional to q/M , provides a charge state spectrum (Figure 2) from which charge state ratios are obtained. An example of the results of this measurement is shown in Figure 3 for ionization of krypton. An analysis of these data was presented this summer at the International Conference on X-Ray and Inner-Shell Physics (Toburen, DuBois and Manson 1982) and will be discussed in the next section.

In the present measurements, we observe target ions that are produced by electron capture as well as direct ionization; for example,

Should the electron be captured or ejected from an inner shell, subsequent relaxation processes can further increase the ion

FIGURE 2. Neon Charge State Spectrum Produced in $\text{H}^+\text{-Ne}$ Collisions

FIGURE 3. Ratio of Multiple/Single Ionization of Krypton by Proton Impact. Dashed curves are theoretical ratios obtained as explained in the next section.

charge state. This is discussed in the following section. During the past year, data were accumulated for noble gas targets for proton energies between 25 and 4000 keV and these are currently being analyzed. We plan to extend these measurements to include simple molecular systems where information on molecular fragmentation will also be obtained.

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INTERPRETATION OF MULTIPLE IONIZATION PROCESSES FOR FAST PROTON IMPACT

L. H. Toburen, R. D. DuBois and S. T. Manson*

A detailed understanding of the processes leading to multiple ionization of target atoms or molecules relies on assimilation of data from a number of sources. In our study of ionization of krypton, we have based our analysis on measured total and partial ionization cross sections (see previous sections, this report), continuum electron emission cross sections, Auger emission cross sections, photoionization cross sections, and calculated inner shell ionization cross sections and Auger branching ratios. In our preliminary analysis of measured partial ionization cross sections, we assumed

that the predominant mechanism for production of multiply ionized species was through inner shell ionization followed by Auger cascade. In the case of ionization of krypton by MeV protons, one can show, using branching ratios from Yin et al. (1974), that an initial 3d vacancy in krypton leads to Kr^{2+} via 3dNN Auger transitions with ~100% efficiency.

Following this procedure, we find that 3p vacancies lead primarily to Kr^{3+} ($M_{2,3}M_{4,5}N + M_{4,5}NN$) and 3s vacancies lead primarily to Kr^{4+} ($M_1M_{2,3}N + M_{2,3}M_{4,5}N + M_{4,5}NN$). One would, therefore, expect the ratio of $Kr^{+1}/Kr^{+2}/Kr^{+3}/Kr^{+4}$ ion yield to be given by the ratio of the respective subshell ionization cross sections. Using subshell cross sections calculated with the Plane Wave Born Approximation (PWBA), we find agreement between the calculated and measured ratio Kr^{+2}/Kr^{+1} to within 20%, the calculated ratio being about 20% low. The calculated Kr^{+3}/Kr^{+1} ratio is, however, nearly a factor of 5 too small and higher charge states show larger discrepancies (see Figure 3 of the previous section). This indicates that either the assumed production mechanism is incorrect or the inner shell cross sections are in error.

In the photoionization work of Krause and Carlson (1966), the yield of Kr^{2+} and Kr^{3+} was found to be nearly equal, which is consistent with our measurements for proton ionization. They attributed the additional Kr^{3+} yield to multiple Auger transitions of the type 3dNNN. Incorporating this mechanism in our analysis gives Kr^{+2} and Kr^{+3} yields of equal value, in agreement with the experiment, but with a magnitude of about a factor of 2 lower than the measurement.

To test the accuracy of the calculated inner shell ionization cross sections, we measured the absolute yield of Auger electrons ejected from the M-shell of krypton; the spectrum for excitation of krypton by 3.67 MeV protons is shown in Figure 1. Cross sections for ionization of the 3d, 3p, and 3s subshells were derived from the $M_{4,5}$, $M_{2,3}$, and M_1 -Auger transition intensities, respectively, after corrections for cascades using the branching ratios of Yin et al. (1974). The location of Coster-Kronig transitions was aided by calculations of Larkins (1973). Subshell ionization cross sections derived from these spectra are shown in Figure 2 along with Born calculations using Hartree-Slater wave functions. Also shown are the total ion yield measurements of DuBois (earlier section of this report). The measured 3d cross section based on Auger intensities is about a factor of 2 smaller than the calculated value. Since multiple Auger processes, i.e., 3dNNN, do not result in discrete lines and are not

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FIGURE 1. M-Auger Spectrum of Krypton Following Excitation by 3.67 MeV Protons. The energy scale is calibrated using the measurements of Werme, Bergmark and Siegbahn (1972) and Coster-Krönig transition is identified using the transition energies of Larkins (1973).

FIGURE 2. Subshell Ionization Cross Sections for Excitation of Krypton by Protons. Solid lines are from a Plane Wave Born Calculation.

included in our estimate, a 50% branching of 3d vacancies to 3dNN transitions would explain the difference between calculated and measured 3d cross sections. A somewhat

larger fraction of 3p vacancies decaying via multiple Auger processes must be postulated to account for the discrepancy observed between calculated and measured 3d cross sections. It is interesting to note that the 3s measurements agree nicely with our calculation. This is particularly interesting because our measured values should be a "lower limit" since there are lower energy transitions (<10 eV) that we cannot observe.

Although preliminary, and with rather large error bars, our measured inner shell cross section data are consistent with the PWBA results if we assume a reasonable fraction of MNNN type transitions. This leaves a question as to why calculated ratios for Kr^{+2}/Kr^{+1} and Kr^{+3}/Kr^{+1} are lower than measured values. One possibility is that multiple ionization occurs initially in a one-step process. Calculations and coincidence measurements are being planned to further investigate this process.

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EXTRAPOLATION OF CROSS SECTION DATA TO HIGHER ION ENERGIES

J. H. Miller, L. H. Toburen, W. E. Wilson and S. T. Manson*

Energy spectra for secondary electrons ejected from atoms and molecules by high velocity ions are needed for track structure calculations. To predict these spectra reliably, we have developed a model for the single differential cross section (SDCS) per unit of energy transfer that is based on Bethe's theory for inelastic scattering of fast charged particles. The model expresses the cross section as the sum of a glancing term that is proportional to the optical oscillator strength of the target plus a hard collision term that predominates when the energy transferred to the target is large.

For small amounts of energy transfer, the hard collisions component deviates strongly from the classical E^{-2} dependence on energy transfer and cannot be neglected relative to the glancing term unless the energy of the projectile is very large. Fortunately, the hard collisions component at small E is only weakly dependent on the projectile. Hence the accurate experimental SDCS for ejection of low-energy electrons by protons with energy near 1 MeV can be used to estimate the hard collisions component in the spectrum at higher ion energies. Predictions

of the model were tested by comparison with experimental SDCS for protons having energy up to 5 MeV, with ab initio Born approximation results for 10 MeV protons, and with measured total ionization cross sections. Results obtained with the model for ionization of helium, neon and argon were recently accepted for publication in Physical Review A.

Dipole oscillator strengths (Zeiss et al. 1977) and branching ratios (Tan et al. 1978) were used to calculate the glancing component in SDCS for ionization of water molecules. Cross section data at 1 MeV were used to deduce the hard collisions component in the spectrum of secondary electrons. The shape of the hard collisions component for ejection of low-energy electrons from H_2O is similar to that found for neon, with a somewhat more narrow minimum between 0 and 10 rydbergs of energy loss. If a "universal" hard collisions component can be deduced from the investigation of a wide variety of targets, then the model can be used to predict the secondary electron spectrum for any target where the optical oscillator strength is known.

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Track Structure

Experimental determination of radiation interactions in small absorber sites is limited to volumes greater than about $0.1\ \mu\text{m}$. This restriction has encouraged the development of computational methods to obtain the desired information in sites of arbitrary size. We are developing Monte Carlo codes to calculate ionization and energy imparted in submicron sites by energetic charged particles. These codes draw on extensive data for electron production in electron- and ion-molecule collisions as the source term for energy degradation calculations. The systematics of molecular cross sections are studied for information on how molecular structure affects energy deposition calculations. We are assessing the reliability of calculations that use gas-phase cross sections to determine energy transport in the condensed phase. To make this assessment, we are comparing calculated multicollision electron spectra with measurements of the corresponding electron spectra emitted from foil targets on proton impact.

ANALYTIC MODEL FOR PRIMARY IONIZATION BY POSITIVE IONS*

W. E. Wilson, J. H. Miller and
H. G. Paretzke**

This effort to obtain a theoretically sound analytical model for delta-ray emission probabilities has been continued. The basic features of the semi-theoretical analytical procedure described last year (Wilson and Miller 1982) have been coded in FORTRAN for inclusion into our Monte Carlo track structure codes (MOCA13). Considerable uncertainty still remains in appropriate asymmetry parameters for the angular distributions since they have not been measured for photoionization of water and our own data (Toburen and Wilson 1977) do not cover a sufficient angular range to determine them accurately. The measured asymmetry parameters for photoionization of methane and neon have not been as useful in this regard as we had hoped. Continuum-charge-transfer has not been modeled in the current algorithm primarily because of the lack of suitable theoretical guidelines.

In order to establish limits of applicability, the current FORTRAN algorithm is being evaluated by comparing it with Bethe-Born theory (Miller et al. 1982). The preliminary indications are that the algorithm will be adequate for track structure simulation of ions up to $\sim 10\ \text{MeV/amu}$. At that point our representation of the separation between glancing and hard collisions appears to break down or at least becomes inadequate. This is short of our goal of $50\ \text{MeV/amu}$ but

is sufficient for many practical high LET radiation fields, e.g., radon and plutonium alpha emitters.

The next direction for extension of our track structure simulation will be lower energy ions. The algorithm described above appears to be realistic down to $\sim 200\ \text{keV}$ for protons, i.e., bare ions. The model does not as yet incorporate any charge exchange processes which become important at these low energies.

As a first step in extension to lower ion energies, we have applied the Rudd formalism (Rudd 1979) to our total ionization data for water vapor (see DuBois et al., this report) by developing a code for fitting the data in the least squares sense. The Rudd formalism is very attractive for modeling purposes because it has a sound theoretical basis, is simple (only two parameters) and therefore computationally convenient. With this formalism we can extend our total ionization cross section algorithm in MOCA13 down to $5\ \text{keV/amu}$. This is, of course, only the first and easiest of several extensions required for "track-end" simulation.

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* W. E. Wilson would like to gratefully acknowledge the cooperation and support of the GSF-Institut für Strahlenschutz, Neuherberg, West Germany, where a portion of this work was done...

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MONTE CARLO SIMULATION OF CHARGED PARTICLE TRACKS

W. E. Wilson and H. G. Paretzke*

With the availability at Pacific Northwest Laboratory (PNL) of more powerful and convenient computational tools, we undertook to

reorganize the structure of MOCA13. The former two codes, MOCA13 and CROSS5, were restructured into a three code set (MOCAION) composed of the original CROSS5 (extended by H. G. Paretzke to 100 keV from 10 keV), which prepares electron transport probability tables; ICROSS4, which does the same for specific energy ions; and a modularized MOCA13, which reads the output from the first two and then generates the actual track interaction coordinates on computer disc files.

These reorganized codes are much easier to work with. Being modularized, new improvements and/or extensions are more easily incorporated. The new algorithm for δ -ray emission, probabilities described in the previous section of this report, has been incorporated into the code ICROSS4.

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Energy Transport

Energy transport studies within the Radiation Physics program are directed toward understanding of the temporal and spatial evolution of potentially harmful chemical species induced in biological materials by energy absorbed from ionizing radiation. Particular attention is given to the dependence of energy transport mechanisms on the quality of the radiation field, since this dependence should provide a basis for understanding quality factors observed in radiation biology. Theoretical energy transport studies use Monte Carlo methods to predict the influence of radiation quality on the yield of reactive intermediates in aqueous solutions. Time-resolved emission spectroscopy is our primary experimental tool for measuring the kinetics of chemical changes induced by radiation with large linear energy transfer (LET).

Fluorescence studies with dilute solutions of benzene in cyclohexane employing pulsed alpha particle and proton beams (West and Miller, 1980) provided the first test of our stochastic model for track structure effects in radiation chemistry (Miller 1981). Unexplained differences between theory and experiment prompted investigations into a new target cell design and the dependence of fluorescence quenching on benzene concentration. The emphasis of our theoretical studies was shifted to aqueous solutions by focusing on track effects observed with pulsed deuteron and alpha particle beams (Sauer et al. 1977). Analysis of these data by a one-radical model showed that the observed dependence of the yield of hydrated electrons on LET was consistent with predictions of our stochastic model (Miller and Wilson 1982). In this report we will discuss our concentration-dependent fluorescence studies and efforts directed toward a multiradical theory of track effects observed using a 3 MeV proton beam stopped in a water jet (Burns et al. 1974).

CONCENTRATION DEPENDENCE OF FLUORESCENCE FROM BINARY LIQUID SCINTILLATORS EXCITED BY PULSED PROTON IRRADIATION

J. H. Miller and M. L. West

Fluorescence decay curves for solutions of benzene in cyclohexane excited by a sub-nanosecond pulse of 1.7 MeV proton irradiation were analyzed by an intertrack quenching model (Miller and West 1977). The model is based on the assumption that transient species (probably cyclohexal radicals) quench excited states of benzene produced in the same particle track. This dynamic quenching process is characterized by two parameters: t_D , the diffusion relaxation time of the track; and α , the product of the interaction radius for quenching and the mean number quenchers per unit track length. In addition to quenching by radiation products, excited states of benzene are also quenched by interaction with solvent molecules. This latter quenching mechanism, which produces exponential fluorescence decay when the liquid is excited by ultraviolet (UV) light, is characterized by model parameter τ .

When fluorescence decay curves for solutions with varying concentrations of benzene were analyzed assuming a concentration independence of τ , a strong dependence of α on benzene concentration was observed (West and Miller 1982). Since the quenching species are most likely products of energy

transferred from radiation to cyclohexane, it seemed unlikely that their yield, expressed through the parameter α , should be strongly dependent on benzene concentration. Hence we were motivated to reanalyze the data allowing both α and τ to depend on benzene concentration.

Results for the concentration dependence of τ are shown by the triangles in Figure 1.

FIGURE 1. Temperature and Concentration Dependence of the Exponential Part of the Fluorescence Decay of Benzene in Cyclohexane Excited by Ultraviolet (UV) Light and Proton Irradiation.

For concentrations of benzene above 0.01 M, the decay of proton-induced fluorescence shows an increase in $1/\tau$ (reciprocal decay time) that is not evident in the UV-induced fluorescence. Unlike our previous analysis, the results shown in Figure 2 suggest

FIGURE 2. Concentration Dependence of Nonexponential Part of the Fluorescence Decay of Benzene in Cyclohexane Excited by Pulsed Proton Irradiation

that α is independent of benzene concentration. These results can be more easily interpreted in terms of our quenching model than the results of our previous analysis with a fixed value of τ . The increase in reciprocal decay time is probably due to the production of excimers, a molecular complex formed by the binding of an excited benzene molecule to another benzene molecule in its ground state. These excimers introduce a new channel for decay of singlet emission that can be readily observed in solutions of benzene in cyclohexane excited by UV light (Birks 1970). Figure 1 suggests that the effect of excimers on the reciprocal decay time becomes more important at a lower concentration of benzene when the liquid is excited by protons than when the liquid is excited by UV light. This interesting possibility could be tested by observing the excimer fluorescence spectrum as a function of benzene concentration.

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DECAY OF HYDRATED ELECTRONS FROM ENERGY DEPOSITED BY 3 MeV PROTONS

J. H. Miller and W. E. Wilson

Hydrated electrons and OH radicals are the principal reactive species formed when energy is deposited by ionizing radiation in an aqueous medium. The spatial pattern of energy absorption events influences the rate of decay of chemical species that results from the energy transferred to the medium. This is considered to be the basic mechanism for the observed dependence of biological effects on radiation quality. At Pacific Northwest Laboratory (PNL) we have developed a technique for treating the nonhomogeneous character of radiation-induced chemistry that makes use of the information provided by detailed Monte Carlo track structure simulation.

Our model of track structure effects in radiation chemistry begins with a reduction of track structure data into functions that describe the mean density of energy near a reactive intermediate at various times after energy has been absorbed in the liquid. For an isolated cluster of reactants, the concentration of energy decreases approximately as $t^{-3/2}$ as the cluster expands due to diffusion. In a high linear energy transfer (LET) track the diffusive expansion of isolated clusters is partially compensated for by the overlap of

neighboring clusters so that the mean energy density decreases approximately as t^{-1} . Neither the spherical symmetry of the isolated cluster nor the cylindrical geometry of the classical high LET track adequately describes the chemical kinetics induced by a 3 MeV proton. This is illustrated in Figure 1 where the decay of hydrated electrons calculated from our Monte Carlo

FIGURE 1. Decay of the Hydrated Electron in Various Types of Track Structure

program is compared with the decay expected for an isolated cluster and a cylindrical track. The LET in the cylindrical track case was taken to be 10 keV/ μ mole, the stopping power of 3 MeV protons in water. Note that at early times our Monte Carlo results are more like the isolated cluster than the cylindrical track. This would be expected since initially the rate of reaction should reflect the small scale track structure. However, as time increases, our Monte Carlo results begin to parallel that expected from the classical cylindrical track model.

In Figure 2 we compare our Monte Carlo calculations with yields of hydrated electrons measured by Burns et al. (1974). Both theory and experiment have been normalized to an initial yield of 4.78 per 100 eV deduced from picosecond pulsed radiolysis with electrons. Agreement between theory and experiment is poor at early times where theory predicts a much more rapid decay than is observed. Part of this discrepancy may be due to experimental uncertainty associated with the deconvolution of the data that is necessary due to limited time resolution. At 10 nsec after

FIGURE 2. Comparison of Decay Kinetics for the Hydrated Electron Predicted by Model with Data of Burns et al. (1974)

irradiation, agreement between theory and experiment is good.

Some refinements in the theory are necessary before detailed comparison with experiment can be made. The theoretical results in Figure 2 are for the initial segment of a 3 MeV proton track. Since the proton beam traverses a water jet whose diameter is nearly equal to the range of a 3 MeV proton, we would expect a significant contribution from protons with higher LET. Track structures for these ions must be calculated and appropriately averaged with the 3 MeV results. This should decrease the yield predicted by theory and increase the deviation between theory and experiment. The source of this discrepancy is unknown at present; however, it is probably due to assumptions made regarding the early track evolution where the theory is most uncertain. It appears from these results that accurate measurements of decay kinetics on a nanosecond time scale can provide a critical test of models for track evolution in liquid systems.

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DOSIMETRY AND BIOPHYSICS

The effects of ionizing radiation on living systems begin with basic physical processes and develop through many stages of chemical reactions and biological responses. The goal of the dosimetry and biophysics program is to utilize the best physical data and mathematical techniques available to characterize radiations, in terms of their interactions with biological material, in a way which will help to predict the final biological response. The stochastic nature of energy deposition along particle tracks and in microscopic sites (microdosimetry) is studied by both experimental techniques and computer simulations. These findings are applied to developing an understanding of the linear energy transfer (LET) and time dependence of cellular response. Furthermore, mathematical models of tissues and organs are combined with microdosimetry to provide more relevant data on the dose to cells at risk in cases of ingested radioactivity.

Modeling techniques developed in the radiation dosimetry and biophysics program are being applied to biological effects of chemical carcinogens in mammalian cells. Although the initial transport of the active agent to sensitive targets in the cell is different for chemicals and radiation, the nature of the damage induced and the cellular response to the damage are similar in many cases.

The radiation dosimetry and biophysics program is an interdisciplinary effort requiring input from many specialties within physics and biology. This is achieved through diverse staff at PNL and by various cooperative and consulting agreements with workers at other laboratories and universities.

Modeling and Cellular Studies

Testing the applicability of mathematical models with carefully designed experiments is a powerful tool in the investigation of the kinetics of the effects of ionizing radiation on cells. Such kinetic studies provide both a means of testing fundamental assumptions regarding the mechanisms of damage and repair and extrapolating to low doses and dose rates to predict effects which cannot be measured directly. Mathematical modeling and cellular studies complement each other. Modeling provides guidance in designing experiments capable of disproving the model, while the experiments themselves provide new input to the model. Based on previous experimental results, the model for the accumulation of damage in *Chlamydomonas reinhardtii* has been extended to include various multiple two-event combinations. Since conventional split dose experiments at low LET cannot discriminate between these models, the effects of combined high- and low-LET radiations have been modeled in a search for a definitive experiment. Stationary-phase mammalian cells are being used to develop a similar type of model for a second biological system. These cells have been shown to be at different points in the cell cycle depending on how they were forced to stop proliferating. Both split-dose and dose-rate experiments are being used to investigate the various damage production and repair processes in these cells.

The goal of our work with chemical carcinogens is to apply concepts developed in radiation biology to obtain a better understanding of the risk associated with exposure to coal-related, chemical pollutants. Our collaboration with the National Center for Toxicology Research through Dr. Robert Heflich has resulted in publication of a model describing the effect of excision repair on the survival of human cells (Miller and Heflich, 1982) and a recent presentation at the 13th International Cancer Congress in Seattle, Washington. This report will give more details on experiments to test this model using repair deficient human cells from xeroderma pigmentosum (XP) patients.

Our experimental studies with chemical carcinogens have focused on the rodent cell line CHO-K1 where replica plating techniques have proved useful in isolating and examining the fate of unrepaired damage in mutants with altered repair capability. A recent publication (Newman 1982) describes a UV-resistant mutant with apparently normal repair activity. More research into the mechanism of this UV resistance and altered response to the carcinogen benzo[a]pyrene-4,5-oxide is presented in this report.

MODELING THE RADIATION RESPONSE OF *Chlamydomonas reinhardtii*

W. C. Roesch

To pursue our goal of establishing quantitative relations between initial physical events produced by ionizing radiation and the subsequent biological effects in cells, we have been developing and testing theoretical models for two kinds of cells, the mammalian Chinese hamster ovary (CHO) cell and the green alga, *Chlamydomonas reinhardtii*. The hamster cell studies are beginning to produce results and will be discussed below. The *C. reinhardtii* studies have been in progress for some time and illustrate the normal scientific cycle of framing, testing, and revising hypotheses.

In our first study with *C. reinhardtii*, we were able to eliminate six competing models for the explanation of its behavior under dose protraction and fractionation. The one model remaining at that time attributed cell killing to an interaction among radiation products that were not themselves lethal.

The number of such products could increase each time a radiation event occurred and could decrease due to processes called "repair". However, this simple model proved inadequate when we extended the experimental conditions: higher dose rates, lower and higher temperatures, and different radiation beams. These changes brought to light new kinetic processes in *C. reinhardtii* and showed these cells are very sensitive to changes in LET of the radiation. To include these new effects in the modeling, we started from the simple model mentioned and included more kinetic steps in the production of the products that interacted to kill the cell. Last year we were led to introduce the idea that three or more radiation products were involved in killing *C. reinhardtii* (two such products seem to be sufficient to explain the behavior of mammalian cells).

This extension of this model leads to a problem: many different kinetic schemes are compatible with our present knowledge about *C. reinhardtii*'s radiation sensitivity. To deal with this problem we are simulating a number of different kinds of experiments

with the models and looking for differences in the predicted results that we can use as the basis for laboratory experiments to distinguish kinetic schemes that may be correct. Last year we reported studying how split-dose experiments change with the doses employed. The changes proved to be different for different models, but the experiments to test the models in this fashion proved to be difficult. This year, at the suggestion of Dr. J. Rasey of the University of Washington, we began studying split-dose experiments in which the two doses are from two radiations with different LETs. In these studies it is necessary to explore not only the differential kinetic schemes but different processes for the production (yield) of the radiation products. We want to study yield relationships, of course, because they bring us even closer to the initial physical events; but they further complicate an already complicated problem.

Figure 1 illustrates what happens for a simple model in such a split-dose, split-quality experiment. The model is the EFG model treated last year (Roesch, Braby and Nelson 1982); it has two independently produced and repaired radiation products and the yields of these products depend on LET in the same way. When both doses are from the same radiation, the curve resembles the

FIGURE 1. An Example of a Split-Dose, Split-Quality Experiment

one we find for *C. reinhardi*. If one dose is from a low-LET and the second from a high-LET (100 times higher) radiation, and each is chosen to give the same survival when the two doses are far separated in time, the curve has exactly the same shape as the first, but it is displaced downward. The same curve is obtained if the order of the two irradiations is reversed. The shape reflects the (unchanged) kinetics. The downward displacement reflects the higher degree of single-event killing by the high-LET radiation; it also makes the effect undetectable experimentally for this radiation. When the production rates of the two products do not change in the same proportion on change of LET, changes in shape as well as changes in magnitude occur (not shown) and may be observable.

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AN ALGORITHM FOR MODELING

W. C. Roesch

The mathematics of the modeling just mentioned is relatively simple. It reduces to handling terms whose Laplace transforms are of the form,

$$\frac{1}{(p+r_1)(p+r_2)\dots(p+r_n)} \quad (1)$$

where p is the transform variable (conjugate to the time, t) and the r 's are positive constants. The solution, a finite series of exponential functions, is well known. Calculations with this solution as the algorithm, however, are inaccurate for small values of t . The solution of Equation 1 starts out as t to the $(n-1)$ th power. Since an exponential starts as the 0-th power, much mutual cancellation of terms is required and ordinary computers are not accurate enough to do it. However, expansion of Equation 1 into an infinite series provides an acceptable algorithm for very small values of t . Unfortunately, if the spread in values of the r 's is very large, a range of intermediate values of t often exists in which neither algorithm works; on a 32-bit computer, errors by orders of magnitude occur.

An algorithm that has not produced such problems starts by dividing the r 's into two groups, those larger and those smaller

than a chosen value--for example $0.1/t$. The factors in Equation 1 with small r 's are combined and expanded into an infinite series. Those with larger r 's are solved with a series of exponentials in the usual way. The two series are multiplied together and then the low powers of t that caused the trouble are cancelled analytically.

The algorithm is slower than those described above, but it need only be used in the intermediate range of t : the selection by $0.1/t$ automatically reverts to one of the previous algorithms outside the intermediate region.

EFFECTS OF LET ON PRODUCTION AND REPAIR OF DAMAGE IN *Chlamydomonas reinhardtii*

L. A. Braby and B. S. Jacobson*

In previous experiments using electron beam irradiation (Braby and Roesch 1978; Nelson, Braby and Roesch 1980) we have established that in *Chlamydomonas reinhardtii* only two-event damage contributes to loss of reproductive capacity and that two or more repair mechanisms modify that damage at normal temperatures. Furthermore, we found that the production of some of the damage is strongly dependent on LET (Braby, Nelson and Roesch 1980). These observations have stimulated extensive modeling activity (Roesch, Braby and Nelson 1982; Roesch, this report) directed toward a more complete understanding of the kinetics of the processes affecting the reproductive survival of these cells. The need for three additional types of data to test aspects of this model is evident. These are:

1. The repair rates for damage produced by higher LET radiations should be checked to determine if they are the same as those for low-LET radiations and, therefore, if the same repair processes may be responsible.
2. The survival curve shape (at high survival) should be checked for a wide range of LETs to see if any single-event component occurs and to determine the relationship between two-event damage and LET.
3. The survival in split dose-split LET irradiations should be checked to see if all radiation products contributing to reproductive death depend in the same way on LET.

All of these experiments require beam segment irradiations similar to those reported previously (Nachtwey and Braby 1975), but with a wider range of LETs than was then available. This wider range of LET can be obtained using $^1\text{H}^+$, $^2\text{H}^+$, and $^3\text{He}^{++}$ ions accelerated by the 2 MV tandem accelerator. However, at the low energies available, the cells must be irradiated in a partial vacuum. Also, in order to do experiments where LET is the only variable, it is necessary to irradiate cells in the same geometry and at the same dose rate for all three beams. Since it is much easier to make negative hydrogen ions than negative helium ions, the normal beam currents differ by several orders of magnitude. In order to obtain suitable dose rates (around 1000 rad/s) and a uniform beam intensity over the irradiated cells, a well-focused beam of ~ 20 nA is passed through a 0.00005-in.-thick nickel foil 1 m before reaching the cells. In this way the maximum available helium ion current can be used while the hydrogen currents can be reduced to suitable levels by defocusing at the injector end of the accelerator. The resulting irradiation facility is illustrated in Figure 1. The dose is monitored by the solid state detector and a preset counter, with a specialized output to operate a shutter in the beam line, controls the exposures. Preliminary experiments using a 3 MeV proton beam show the expected split-dose effect, but were hampered by slow recovery of the beam line vacuum when the dishes of cells were installed. Increased pumping capacity is being installed to overcome this problem.

FIGURE 1. Schematic of the Beam Line for Positive Ion Irradiation of Cells

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KINETICS OF PLATEAU-PHASE MAMMALIAN CELLS

J. M. Nelson, N. F. Metting and L. A. Braby

We have previously described two techniques used to stop exponential growth in monolayer cultures of Chinese hamster ovary (CHO) cells (Nelson 1978; 1979). These techniques permit termination of continued population expansion and entrance into plateau phase. If cell proliferation ceases as well, these cells are said to have entered stationary phase. Generally, individual cells exit the growth cycle somewhere after division, but prior to replicating their genetic material. Such post-mitotic G_1 -phase stationary-phase cells are referred to as G_0 -phase cells after the nomenclature introduced by Lajtha (Lajtha, Oliver and Gurney 1962; Lajtha 1963). However, more recent evidence indicates that stationary-phase cells may also exit the cycle elsewhere. For example, plateau-phase cells subjected to severe nutritional stress (or possible exposure to toxic metabolic by-products) as a consequence of starvation, cease proliferation by exiting the cycle after completing DNA

synthesis but before dividing. These G_0 -phase stationary cells enter and pass through mitosis within 3 to 5 h after harvest by trypsinization and replating.

Growth kinetics of both contact-inhibited (fed) and nutritionally deprived (starved) cell populations growing into plateau phase, as well as after release from plateau, have been measured by several techniques. Both the induction of mitosis and its relative frequency as a function of time after release differ considerably from one type of plateau cell to the other. These differences have been described previously (Nelson 1978; 1979). The behavior of these cell populations with respect to DNA synthesis has also been found to differ considerably depending on the means by which the plateau has been reached. Such striking differences were surprising since both of these populations appear morphologically similar. They are perturbed populations of resting cells, probably representative of the normal situation *in situ*. Their different behavior patterns are in response to the different stimuli associated with the plateau induction.

Thymidine labeling indices have been determined by autoradiographic methods and used to evaluate changes in the fractions of cells involved in *de novo* DNA synthesis in exponentially growing populations as they enter plateau phase. In addition, pulse-labeled cells were used to evaluate DNA-synthetic activity by measurement of changes in thymidine incorporation rates.

As seen in Figures 1 and 2, little difference may be observed between starved and fed cultures over the first week or so. However, profound differences develop as these cultures progress beyond this age. The labeling index shown on the left side of each figure is a measure of the fraction of cells in S-phase that are actively synthesizing genetic material. In nutritionally deprived populations, this fraction falls precipitously, beginning on about the third or fourth day of passage. These cells enter the population-density plateau perhaps a day later, on the fourth or fifth day. This fall continues, interrupted only by a short plateau between the tenth and fifteenth day. This plateau may represent the minimum activity displayed by viable cells. Following this plateau, the index again falls to a level below the limits of practical measurement, probably due to cytolysis leading to extinction of the culture. Although the mean rate of DNA synthesis (as seen in the right side of Figure 1) reflects this initial sudden drop in activity following the short plateau, the amount of material

FIGURE 1. The Fraction of Cells Synthesizing DNA and the Average Amount of Synthesis per Cell in Plateau-Phase Cultures Induced by Nutritional Stress, Plotted Against Time After Passage

FIGURE 2. The Fraction of Cells Synthesizing DNA and the Average Amount of Synthesis per Cell in Plateau-Phase Cultures Induced Spontaneously by Contact Inhibition, Plotted Against Time After Passage. The arrows indicate Monday morning "feedings". The growth pattern during the 3 days preceding this feeding is similar to that of starved populations as seen in Figure 1.

synthesized decreases more slowly, suggesting that surviving cells are synthesizing DNA more actively.

The dramatic fall in DNA synthesis observed in starved cells is not seen in those plateau-phase cultures induced by contact inhibition. The thymidine labeling index illustrated in Figure 2 appears to fall less than an order of magnitude and remains at this depressed level for an extended period, albeit with considerable unexplained variability. More recent analysis of these data in collaboration with Paul W. Todd of Pennsylvania State University has shown that the labeling index of this type of plateau culture has been depressed to about one-fifth that found normally, principally because of a highly variable increase in the length of G₁-phase. At the same time, the cell generation time has also been significantly lengthened, giving rise to the ever greater suppression of thymidine incorporation rate seen on the right side of Figure 2.

We now believe that these contact-inhibited cells never actually become stationary. If they were to receive relatively constant medium refreshment in order to maintain adequate nutrition, we would expect synthetic activity to fall to about 20% of that found in exponentially growing populations and remain there. However, medium was refreshed only every two or three days (M, W, F feeding). Since these cultures are maintained at considerably higher densities than starved cultures, their response to nutritional stress should be correspondingly faster. Synthetic activity, as an indicator of proliferative activity, falls rapidly over the 72-h interval preceding the Monday morning feeding in the same way as that observed in starved cells and illustrated in Figure 1. The variation in DNA synthesis, both in the amount of synthesis and the fraction of cells involved, has been found to reflect both the growth attenuation caused by contact inhibition and the sudden periodic fluctuations corresponding to loss of nutritional integrity of the culture medium between changes.

Additional studies identify changes in clonogenic potential and viabilities (by dye-exclusion techniques) of both nutritionally deprived and contact-inhibited cells after a period of severe depression. Results of these studies are summarized in Figure 3. Although reproductive survival is affected by growth attenuation resulting from contact inhibition, these cultures retain much of their potential. In contrast, starved cells are not able to withstand the stress for very long and expire sometime around the sixteenth day. Cultures derived from a single original plate die at roughly the same time, although

the survival time of different groups may vary. This is probably due to slight variations in growth rate as a consequence of a variety of unknown factors. As seen in Figure 3, cell death (as defined by loss of dye-exclusion ability) occurs simultaneously with loss of clonogenic potential.

FIGURE 3. Viable Cell Fractions Determined by Erythrosin-B Dye-Exclusion Techniques, and Clonogenic Potential Normalized at the Maximum Values, for both Nutritionally Deprived (Starved) and Contact-Inhibited (Fed) Cell Populations, Plotted Against Time After Passage

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SPLIT-DOSE REPAIR IN MAMMALIAN CELLS

J. M. Nelson, L. A. Braby and W. C. Roesch

Sublethal damage repair has been found in many cell systems, but can be quantitated only in systems possessing constant radiation sensitivity. Certain types of plateau-phase mammalian cells may be used to quantitate sublethal radiation damage repair because radiation sensitivity under conditions of stationary growth does not vary with time.

We have previously described techniques for producing monolayers of plateau-phase cells (Nelson 1978; 1979), and last year reported preliminary experiments to assess slower repair processes in Chinese hamster ovary (CHO) cells. Additional experiments have been performed in an effort to clarify these findings.

As with previous studies of sublethal damage, survival data were analyzed according to our Accumulation of Damage Model (Nelson, Braby and Roesch 1979; Nelson, Braby and Roesch 1980). The details of this model, which considers exponential repair of the two-event or sublethal component of damage, have been described elsewhere (Roesch 1978; Braby and Roesch 1978). The model predicts that when the survival data are plotted as the logarithm of $\ln(S_1 S_2 / S)$ against time between doses (where S_1 and S_2 are survivals after two doses given independently, and S is the net survival after both doses), the data should fall on a straight line. The mean repair time is the negative reciprocal of the slope of this line. Furthermore, if more than one repair process exists, data for each may be separated by subtraction in much the same manner as that used for separating mixed radioisotopes having different half-lives.

We have also shown that plateau-phase mammalian cells stop cycling at various points within the proliferative cycle, not simply as G_0 -phase cells exiting after mitosis and re-entering the cycle prior to DNA-synthetic phase. The specific age at which these cells become quiescent depends on the method by which stationary phase has been induced. Nutritionally deprived cultures are found to contain predominantly cells that exited the cycle in G_2 -phase and reside there as stationary cells until released by enzymatic harvest. In contrast, contact-inhibited cultures probably never become truly stationary. Rather, their growth rate is greatly attenuated. Due to a lengthening of G_1 -phase, the number of cells resident there is increased, but slowly cycling cells are found throughout the cell cycle.

Split-dose survival studies to assess sublethal damage repair have been done with each of these kinds of cells. Results of these studies have been summarized in Figures 1 and 2. We find a correlation between both the radiation sensitivity (Figure 1) and the characteristics of the repair processes (Figure 2) with the age distributions within the two populations. Cells in G_2 -phase are known to have greater sensitivity to radiation than asynchronous populations. This is in agreement with the

FIGURE 1. Split-Dose Survival as a Function of Interfraction Interval for Both Contact-Inhibited (Fed) and Nutritionally Deprived (Starved) Plateau-Phase Cells. In each case, undisturbed plateau-phase plates were irradiated with 2 equal fractions (400 rad each) separated by varying intervals. S_m is the hypothetical maximum survival that would result if two fractions were separated by an infinite time interval, and is normally estimated by the product $S_1 S_2$. In this case, S_m was taken from the asymptote of the actual survival which is fitted by eye with the solid line.

FIGURE 2. The Same Data Seen in Figure 1, Plotted as $\ln(S_m/S)$ Against the Interfraction Interval. When plotted in this way, survival data enhanced by a single repair process should fall on a straight line. The negative reciprocal of the slope of this line is the mean repair time (τ) of the single process.

data shown in Figure 1, where the nutritionally deprived cells, most of which are in G₂-phase, demonstrate a lower survival to the same dose as that given to the contact-inhibited cells.

Analyses of the split-dose data, plotted as $\ln(S_1S_2/S)$ in Figure 2, indicate other differences. Contact-inhibited cells demonstrate evidence for sublethal damage repair, although only part of the damage appears to be repaired. That damage not repaired within the first 5 h appears not to be repaired at all. Starved cells, on the other hand, repair considerably more damage but at a slower rate than the fed cells.

These data are preliminary and require clarification, both in terms of improved statistics and better control over timing to eliminate possible effects of repair of potentially lethal damage. Consequently, a computer-controlled dispensing pipetter that is capable of greatly improved precision during clonogenic cell assay procedures has been developed and built. This equipment also permits the handling of about five times the quantity of plates per experiment. The improved plating precision should reduce the scatter in experimental points, and the increased number of plates allows for duplicate irradiations to determine the extent of biological variability or for additional interfraction intervals to investigate multiple repair processes.

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DOSE-RATE EFFECTS IN STATIONARY-PHASE MAMMALIAN CELLS: TESTING THE ACCUMULATION MODEL

N. F. Metting, W. C. Roesch, J. M. Nelson and L. A. Braby

In the past we have irradiated the green alga *Chlamydomonas reinhardi* to study sublethal damage repair mechanisms by means of split-dose and dose-rate experiments. Results with *C. reinhardi* were accurately predicted by the Accumulation Model (Braby and Roesch 1978). It has now become possible to test the model on another, more complex life system, cultured mammalian cells.

Characterization of nutritionally inhibited, stationary-phase Chinese hamster ovary (CHO) cells indicates a very low, stable rate of DNA synthesis for cultures over 10 days old (Nelson, Braby and Metting 1982). More recent work suggests an upper age limit of 15 days to insure adequate plating efficiencies necessary to the assay (Nelson, Metting and Braby, this report). This 5-day period of unchanging radiosensitivity is sufficient for conducting low dose-rate experiments. A series of these experiments were done using 250 kV X-rays at four dose rates between 1 and 100 rad/min; from 4 to 8 different doses were given for each dose rate. Survival was determined by clonogenic assay.

In Figure 1, standard survival curves, i.e., the logarithm of survival versus dose, are shown for the four dose rates. A pronounced dose-rate effect is evident, indicating that repair is occurring in these cells. Figure 2 shows the data replotted as $\ln[(-\ln S)/D^2]$ versus t , the period of irradiation. Lines have been drawn to estimate a best fit for each of the dose rates. There are two possible explanations for these results.

Figure 3 shows the theoretical effect (as predicted by the Accumulation Model) of holding dose rate constant for low dose rates. The solid line illustrates the case of negligible single-event killing; the dashed lines are combined single-event and two-event damage at various dose rates. As

FIGURE 1. Survival of Starved CHO Cells Irradiated at Different Dose Rates. The lines were fitted by eye and a single line was used for the 16 and 100 rad/min groups.

FIGURE 2. The Data from Figure 1 Plotted in a Way that Simplifies Analysis in Terms of Damage Production and Repair

FIGURE 3. Theoretical Curves for Arbitrarily Chosen Factors Plotted in the Same Way as in Figure 2. According to the accumulation of damage model, data from cells with only two-event damage (—) will fall on a single curve independent of dose rate. Data from cells with single-and two-event damage (---) will produce different dose-rate dependent curves.

the dose rate becomes smaller, the curves tend to become straight, sloping, parallel lines because repair is eliminating the two-event component of the damage. It may be that in plateau-phase CHO cells both single-event and multiple-event (sublethal) damage and damage repair occur, but that the single-event component masks the other at very low dose rates. A second explanation might be that only single-event damage, and therefore single-event damage repair, is occurring in this biosystem. This repair would be proportional to one-half of t , the irradiation period, so survival would be higher at low dose rates.

Analysis of these results has suggested additional experiments designed to quantify single-event repair mechanisms in our mammalian cells.

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CORRELATION OF SURVIVAL AND EXCISION RATE IN REPAIR DEFICIENT HUMAN CELLS

J. H. Miller and R. H. Heflich*

Cells from human xeroderma pigmentosum (XP) patients show enhanced sensitivity to ultraviolet (UV) light and chemical carcinogens relative to normal fibroblast (NF) (Maher and McCormick 1976). The assumptions that survival reflects the extent of chemical alteration of DNA at some time after exposure when damage is fixed by cellular metabolic processes and that prior to fixation excision of damage obeys first-order kinetics lead to quantitative correlation between the asymptotic slope of the survival curve and the rate of excision of carcinogenic residues from DNA (Miller and Heflich 1982). By applying this concept to the survival of XP cells from complementation groups C and E, we concluded that XPE cells should excise adducts of N-acetoxy-2-acetyaminofluorene (N-AcO-AAF) at a rate that is ~60% of the rate of excision of these adducts by NF. Similarly the rate of excision by XPC cells was predicted to be 40% the normal rate. Figure 1 shows the result of experiments designed to test these model predictions. The fraction of bound residues of N-AcO-AAF is plotted as a function of hours after treatment. Lines show the result of regression analysis. As expected from our model, the lifetime of residues on the DNA of XPE cells is about

FIGURE 1. Kinetics of Excision Repair of Residues of the Carcinogen N-Acetoxy-2-Acetyaminofluorene (N-AcO-AAF) by Normal Fibroblasts (NF) and by Fibroblasts from Xeroderma Pigmentosum (XP) Patients in Complementation Groups C and E

twice as large as the lifetime in NF. However, the lifetime of residues in XPC cells is considerably longer than that expected from survival data.

One possible explanation for the observations with XPC cells is that their uptake of the carcinogen is different from NF, resulting in higher survival for the same concentration of carcinogen in the growth medium. To test this hypothesis we applied our model to UV data where differences in the initial amount of damage for the same fluence are unlikely. Again from the UV survival data our model predicted that XPC cells should excise UV-induced damage with a rate that is 40% of the normal rate. Figure 2 shows the results of the data analysis on the removal of UV-endonuclease-susceptible sites by XPC and NF (Zelle and Lohman 1979).

As was the case for N-AcO-AAF, the lifetime of UV-induced damage in the DNA of XPC cells is much longer than expected on the basis of the dose-response for survival. Hence, we feel that a difference in initial damage is not a likely explanation for these results. Other explanations currently under investigation include: 1) more time available to XPC cells for repair, and 2) variations in rate of excision during cell growth make quiescent repair rates a poor determinate of survival.

FIGURE 2. Kinetics of Excision Repair of Damage Induced by Ultraviolet (UV) Light in Normal Fibroblasts (NF) and by Fibroblasts from Xeroderma Pigmentosum (XP) Patients in Complementation Group C (XPC)

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EFFECTS OF SERUM ON THE DOSE RESPONSE FOR SURVIVAL OF CHINESE HAMSTER OVARY CELLS AFTER EXPOSURE TO BENZO[a]PYRENE-4,5-OXIDE

C. N. Newman and J. H. Miller

The survival of Chinese hamster ovary cells, strain CHO-K1, treated with benzo[a]pyrene-4,5-oxide (BaP-4,5-O) in a growth medium that contained 10% fetal calf serum is shown in Figure 1. The fraction of surviving cells is plotted as a function of the product of the concentration of carcinogen in micromole (μ mole) and the exposure time in hours. Exponentially decreasing survival is observed when the cells are treated with 6 and 12 μ mole of BaP-4,5-O for various exposure times; however, a shouldered dose response, frequently considered as indicative of repair, is measured when cells are exposed for 3 h to various concentrations of carcinogen.

FIGURE 1. Cell Inactivation by Benzo[a]pyrene-4,5-oxide. Cells were exposed in growth medium to various concentrations of carcinogen for 3 h (●) or to 6 μ mole (■) or 13 μ mole (□) of carcinogen for different exposure times. The total exposure along the abscissa is the product of chemical concentration and exposure time (COT).

A model to explain these seemingly contradictory observations can be formulated under the hypothesis that Chinese hamster ovary (CHO) cells do not excise a significant fraction of damage initially induced by the treatment. Assuming that each carcinogen residue covalently bound to DNA has a probability α of inactivating the reproductive capacity of the cell and denoting by $k(C,t)$ the rate of binding at time t after a concentration C of BaP-4,5-O has been added to medium, the survival $S(C,T)$ after exposure for a time T is given by

$$-\ln S(C,T) = \alpha \int_0^T k(C,t) dt \quad (1)$$

The exponential decrease in survival observed when T is varied at a fixed value of C can be explained in this model by the hypothesis that the rate of binding is independent of the previous exposure to the carcinogen (i.e., k is not a function of t). Hence Equation 1 reduces to

$$-\ln S(C,T) = \alpha k(C)T \quad (2)$$

However, the rate of binding is not simply proportional to the initial concentration in the growth medium because this would imply that S is a function of the product of C and T only, which Figure 1 shows is not the case.

The rate of binding to DNA depends upon the interaction of BaP-4,5-O with components of the medium and on the mechanism of transport into the cell nucleus. Sufficient information in these areas is not presently available to speculate on the functional form of $k(C)$; however, if our model is correct, the dose-response for survival can be used to empirically investigate the dependence of binding rate on the concentration of carcinogen in the growth medium. In some cases it may be possible to test the empirically derived relationship by actual measurements of binding.

Solving Equation (2) for $k(C)$ we obtain the result

$$k(C) = \frac{\ln(S)}{dT}$$

Figure 2 shows a plot of $-\ln(S)/T$ as a function of initial concentration of BaP-4,5-O. The open circles show results based on the survival data in Figure 1 where the growth medium contained 10% fetal calf serum. The closed symbols show results obtained from survival measurements when cells are treated in a serum-free medium. The intercept of the asymptote with the concentration axis can be interpreted as a threshold concentration of BaP-4,5-O where

FIGURE 2. Lethal Damage Induction Rates by Benzo[a]pyrene-4, 5-oxide. The natural logarithm of the reciprocal of the surviving fraction was divided by the exposure times, T , and plotted against concentration of carcinogen for cells exposed in growth medium (open circles) or in serum-free growth medium (closed symbols). Exposure times were 2 h (■), 3 h (▼) or 5h (●).

effective binding to DNA begins. The presence of 10% fetal calf serum in the medium appears to cause a threshold dose of about 5 μ mole. The mechanism for this effect is probably the strong affinity of the carcinogen for a liquid component of the serum.

POOL SIZES IN AN ULTRAVIOLET (UV)-RADIATION-RESISTANT MUTANT OF CHINESE HAMSTER OVARY CELLS

C. N. Newman

Unusual biological and biochemical properties of a repair-proficient Chinese hamster ovary cell mutant, Mut 8-16, described in last year's report (Newman 1982a) have been published (Newman 1982b). Briefly, that study indicated the presence of an heretofore unreported DNA repair mode in mammalian cells which appears to make a significant contribution to either survival and/or mutation-induction (depending upon the particular carcinogen) at low-level exposure doses. Since that report, a strong effort to elucidate more specific details concerning the molecular basis of repair in Mut 8-16 has ensued. A significant discovery was that Mut 8-16 maintained an abnormal deoxynucleotide triphosphate (dNTP) pool balance in comparison to its parent cell, CHO-K1. These results were first suspected when an unusual sensitivity of Mut 8-16 to the DNA polymerase-specific antibiotic, aphidicolin, and to cytosine-1- β -D-arabinofuranoside (ara-C) was observed (Figure 1). These antibiotics compete with deoxycytidine triphosphate (dCTP) for binding to the polymerase molecule (Huberman

FIGURE 1. Sensitivity of CHO-K1 (●, ○) and Mut 8-16 (■, □) to Aphidicolin (●, ■) or Ara-C (○, □).

1981); therefore, these observations strongly suggest an increased affinity for the inhibitors resulting from either a reduced dCTP pool (i.e., less competition) or an alteration in the polymerase molecule itself. In addition, analysis of DNA obtained from cells exposed to the radioactive form of the DNA precursor thymidine (TdR) (shown in Table 1) indicated that the TdR and/or thymidine triphosphate (TTP) pool was inordinately increased in Mut 8 roughly by two to threefold since the specific radioactivity of the radiolabeled DNA was consistently low by this factor in comparison to that obtained from CHO-K1. These findings prompted direct measurements of dNTP pools in mutant and parent cell lines; these measurements are illustrated in Table 2. Both a significant reduction in the dCTP pool and a 2.5-fold enlargement of the TTP pool in Mut 8-16 were observed, consistent with the previous observations (Figure 1, Table 1). How a pool imbalance in Mut 8-16 might affect cellular responses

TABLE 1. Specific Activities of Radiolabeled DNA

Expt Cell	¹⁴ C-dpm ^(a) per cell	Parental ^(b)		de novo DNA ^(c) 3H-dpm/Å ₂₆₀
		¹⁴ C-DNA dpm/Å ₂₆₀	CHO-K1 ¹⁴ C-dpm Mut 8-16 ¹⁴ C-dpm	
1 CHO-K1	—	55249	2.28	1.9 x 10 ⁶
Mut 8-16	—	24251		2.1 x 10 ⁶
2 CHO-K1	—	73873	2.45	1.05 x 10 ⁵
Mut 8-16	—	30188		1.08 x 10 ⁵
3 CHO-K1	3.9 x 10 ⁻⁴	—	2.44	—
Mut 8-16	1.6 x 10 ⁻⁴	—		—
4 CHO-K1	—	103558	3.87	—
Mut 8-16	—	26740		—
5 CHO-K1	—	169082	3.26	—
Mut 8-16	—	51737		—

(a) Obtained from whole cells grown as in (b).

(b) Obtained from alkaline CsCl equilibrium gradients of partially purified cell extracts. Cells were grown 1-3 days in F-12 w/o TdR + 10% FCS or 10% dialyzed FCS + ¹⁴C-TdR, 57 mCi/mmol, 0.0188 µCi/ml.

(c) Medium from (a) was replaced with F-12 w/o TdR, 10⁻⁴M BrUdR, 10⁻⁶M FUdR, 10% dialyzed FCS, ³H-TdR, 1 or 10 µCi/ml, 20 Ci/mmol, then cells were chased 1 h in same medium w/o ³H-TdR.

TABLE 2. Deoxyribonucleotide Triphosphate Pools^(a)

Cells	dATP	dGTP	dCTP	dTTP
CHO-K1	11.1	0.678	18.8 ± 0.6	2.18 ± 0.65
MUT8-16	9.8 ± 0.5	0.665	12.5 ± 1.6	5.6 ± 1.6

(a) Methanol and perchloric acid extracts of exponentially grown cultures were analyzed enzymatically for dNTP pools using *E. coli* polymerase, a corresponding synthetic DNA copolymer [poly(dA-dT) or poly(dI-dC)] and incorporation of acid insoluble ³H-deoxynucleotides. Results are expressed in pmol/µg DNA. Where indicated, errors represent one standard deviation.

to carcinogen is presently under investigation. The activity of poly (ADP-ribose) polymerase is known to be affected by a dCTP/TTP pool alteration (Meuth 1981) and to be important in effecting DNA repair (Nduka, Skidmore and Shall 1980), probably by ligation of partially repaired DNA following exposure of cells to chemical and radiation insults (Creissen and Shall 1982). The activity and role of this enzyme in response to DNA damage in Mut 8-16 are now being studied in depth.

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EFFECTS OF CELL DENSITY ON THE SURVIVAL OF CHINESE HAMSTER OVARY (CHO) CELLS EXPOSED TO BENZO[a]PYRENE-4,5-OXIDE

C. N. Newman

A variable intrinsic sensitivity of mammalian cells to benzo[a]pyrene-4,5-oxide was observed, and was found to depend upon the culture density during the exposure phase of the experiment. The effect of density on survival following exposure to carcinogen is shown in Figure 1. The same approximate 8% survival levels (measured when cells were replated at 8-15 cells/cm²) are obtained with cultures having up to 10⁴ cells/cm². At densities up to 1.33 x 10⁵ cells/cm² (confluence), however, there is a substantial loss or absence in sensitivity to the killing effects of this treatment. These results were not due to the accumulation of metabolites in the medium or changes in pH (not shown). Figure 2 illustrates that survival did not increase significantly up to eight days following exposure as long as cells were grown and periodically replated at densities of at least 6.6 x 10³ cells/cm², even though the generation times of the exposed cultures were normal (14.5 h) indicating that all cells were growing under these conditions. These results suggest the presence of protective neighbor cell interactions when cells are in relative proximity to one another, such as is found in whole animal tissue. In addition, these findings imply that extraordinary care be exercised when designing and interpreting experiments with carcinogens and cultured cells.

FIGURE 1. Effects of Cell Culture Density on Killing. Cells were exposed for 24 h to 6 μmole (triangles) or 3 h to 2 μmole (circles) of benzo[a]pyrene-4, 5-oxide in a complete growth medium or in a serum-free medium, respectively, at the indicated initial culture densities. The medium was then removed and cultures were either incubated directly in fresh, complete medium, (closed symbols) or trypsinized, then plated at cloning densities in fresh complete medium (open symbols) for 7 days, when clones were counted and survival levels determined.

FIGURE 2. Effect of Exposure and Post-Exposure Cell Densities on Survival. Cells were exposed to carcinogen at the indicated culture densities in a complete medium as described in Figure 1. At periods after exposure, cultures were trypsinized and subcultured at the cell densities shown in parentheses. The dashed line represents the expected increase in survival of 6.6×10^3 cells/cm² following exposure if only survivors divide, based upon increases in cell numbers as measured by an electronic particle counter (not shown) and an expected generation time of 14.5 h. Solid lines are approximate fits to the corresponding data points.

Dosimetry

Projects in dosimetry and cellular effects are closely integrated and have the mutual purpose of exploring the connections between the primary physical events produced by radiation and their biological consequences. Dosimetry concentrates on the physical aspects of this problem, ranging from the use of cross-section data to calculate the energy deposition pattern for charged particle tracks to the design of irradiation facilities required to make specific exposures to test biophysical models.

ENERGY DEPOSITION BY DELTA RAYS

F. C. Weigand* and L. A. Braby

Quantitative interpretation of the biological effects of different high LET radiations relies on a suitable description of the differences in the energy deposition patterns of these radiations. There are no experimental techniques with sufficient spatial resolution to measure these patterns, so they must be determined by Monte Carlo calculations. The Monte Carlo method, though time-consuming, would be quite reliable if all of the physical processes and cross sections involved were known. Unfortunately, this is not the case even for energetic protons interacting with simple molecules, much less for more complex projectiles such as H_2^+ or He^{++} . Typically, track structure models are developed using the best data available and the results are then compared with various experimental results. One good experiment for this purpose is the measurement of energy deposition in a small cylindrical site by primary charged particles that pass near the site but do not intersect it.

Experimental measurements for protons (Glass and Roesch 1972) have been compared with Monte Carlo calculations for proton tracks (Wilson and Paretzke 1980) and the results are in good agreement, helping to confirm those calculations. The calculations are now being extended to projectiles with more complex electronic structures which add additional delta ray production processes. In addition, ions such as H_2^+ and He^{++} are being used for biological experiments which will require more detailed knowledge of the energy deposition patterns. For these reasons the experimental apparatus originally used by Glass and Roesch has been fitted with a new collimator and preamp and is being installed on the 2 MV van de Graaff. Tests of the detector gas gain and resolution are underway.

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RADIATION DOSIMETRY

W. C. Roesch

In 1980, the National Council on Radiation Protection activated a scientific committee (SC #52) under the chairmanship of Dr. H. H. Rossi of Columbia University to prepare a broad analysis of the principles of dose calculations. As part of our contribution to the work of this committee, I made a mathematical analysis of simple radiation fields that is useful in discussing the region of applicability of ordinary radiation dosimetry.

When irradiation is by radionuclides deposited in a tissue, the radiation is often very nonuniform because of nonuniform deposition and because of agglomeration of the active atoms into particulates. Usually the actual distribution is not known. It has been customary in these internal depositions, for lack of anything better, to correlate the observed effect with the absorbed dose that would have existed in the tissue had the activity been uniformly distributed. The question of just how good or bad the assumption of uniform deposition is has not been answered. This and related questions are called by some the field of "minidosimetry."

While developing the application of microdosimetry to internally deposited radionuclides (Roesch 1977), I showed how the nonuniformity of deposition could be coupled with the statistical matters of concern in microdosimetry, thus simply avoiding the assumption of uniform deposition.

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In order to deal with the minidosimetry question, I considered only one-dimensional fields and showed that the Fourier transform of the dose distribution equaled the product of the transform of the activity distribution and the transform of the dose distribution due to a plane source of unit activity and suitable distribution of emission angles. Enough information exists in the literature about plane sources to determine or estimate this last factor. For simplicity in calculation, I chose to compare sinusoidal activity distributions with the uniform distribution; this choice should be adequate for understanding real distributions. Figure 1 shows typical results. The solid line is the activity distribution. The long-dash, short-dash line is the dose distribution that would result if the same activity were uniformly distributed. The dashed line is the dose distribution for a radiation of short range compared to the oscillations. The dose at a point is due to particles emitted within range of the point; thus short-range particles must follow the activity distribution closely. The dotted line is the dose distribution for a radiation of long range. The penetration of the particles attenuates the effect of the oscillatory source.

For more specific calculations the question was asked: what fraction of the cells in

FIGURE 1. Examples of How the Dose Due to an Oscillatory Source Differs from the Dose if the Same Activity were Uniformly Distributed. The activity distribution (—); the dose distribution if the same activity were uniformly distributed (— · —); the dose for a source of short-range particles (---); the dose for a source of long-range particles (····).

the tissue is exposed to a dose within a specified percentage (25% was used) of the dose that would have existed if the same activity were uniformly distributed? For almost all beta-ray sources, nearly all the cells were within the 25% of the uniform dose. But for all alpha-particle sources, only 16% of the cells received doses within 25% of the uniform dose. (A limit of 16% is reached for all short-range particles.)

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RE-EVALUATION OF THE HIROSHIMA-NAGASAKI RADIATION DOSES

W. C. Roesch

In 1976, Dr. H. H. Rossi of Columbia University described to the National Council on Radiation Protection (NCRP) some new calculations that he and his colleagues had made based on the doses received by the survivors of the atomic bombings at Hiroshima and Nagasaki. On the basis of these calculations he recommended the NCRP lower its permissible doses for neutrons. [This recommendation was later published with Mays (Rossi and Mays 1978)].

One of the responses of the NCRP was to set up a Task Group on Atomic-Bomb Dosimetry, under the chairmanship of Dr. H. O. Wyckoff of the NCRP, to review the dosimetry for the data on which the recommendation was based. The Task Group, to which I was also appointed, began its work in 1976 and held a number of meetings with the staff at Oak Ridge National Laboratory who had made most of the original dosimetry studies. The Task Group finally concluded that the material in the literature and in published laboratory reports was insufficient for a scientific review of the dosimetry. The main problem was information that was missing because it was classified SECRET. The Task Group recommended that a person with proper security clearance should dig into the classified and unclassified reports to assemble the necessary information. Their hope was that a satisfactory part of the result might now be declassified and released to the general public.

The recommendation was passed on to the Department of Energy (DOE), which responded by funding Dr. G. D. Kerr of Oak Ridge to undertake the task. Kerr began in September 1979. He not only searched the early literature but inquired about recent research that was relevant and was thus led to draw a number of other investigators into the study (Kerr 1981).

Independently of Dr. Kerr et al. and of the NCRP Task Group, W. E. Loewe and E. Mendelsohn of the Lawrence Livermore Laboratory had been impressed by the controversy over permissible neutron doses and its potential impact on nuclear activities. They employed radiation transport computer codes they had been using in other work to re-examine the dosimetry of the survivors (Loewe and Mendelsohn 1981; 1982).

These activities came to the attention of the general public early in 1981 when a symposium on the re-evaluation of the doses was held at the annual meeting of the Radiation Research Society (Sinclair and Failla, 1981). Many articles began to appear in the scientific and lay press. I gave a number of lectures about what was happening (Roesch 1981a; 1981b; 1982a; 1982b).

That fall DOE held a symposium of the involved scientists to help map out what needed to be done to make a proper re-evaluation. DOE then set up a program involving several of its laboratories to conduct the re-evaluation. They engaged Dr. R. F. Christy, Chancellor of the California Institute of Technology and an early weapons expert, to head the program. Because the Japanese are very interested, DOE requested the National Academy of Sciences, which has the legal responsibility for relations with the Japanese in studies concerning the bombings, to set up a committee to oversee Christy's program and to deal with the Japanese. Dr. F. Seitz, president emeritus of Rockefeller University and of the National Academy of Sciences, was chosen as the chairman. He is being assisted by Drs. S. Jablon and W. H. Ellett of the Academy staff. The organizational meeting of this Panel on Reassessment of A-Bomb Dosimetry was held in July with action meetings to start early in the fall.

At best, it will be a year or two before the re-evaluation is complete.

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• Microdosimetry of Internal Sources

The purpose of this study is to develop practical methods for calculating microdosimetric distributions of plutonium or other alpha-emitting elements that are deposited, especially as particulates, in soft tissue and lung tissue. This study will aid the correlation and extrapolation of radiation effects measured at different levels of exposure and in different species. Computational methods will be developed and tested in the Radiological Physics Section. Concurrently, the Dosimetry Technology Section will develop cell and tissue models in which those methods will be applied.

LUNG MICRODOSIMETRY CALCULATIONS

W. C. Roesch

In lung microdosimetry calculations one needs the probability of finding a particulate, an emitter of radiation, as a function of distance from a target site. We assume the particulates lie on alveolar walls and, thus, calculate this probability from three others that we can measure: 1) $h(t)dt$, the probability of a tissue thickness, t , between the site and the next alveolar wall; 2) $g(v)dv$, the probability of a distance, v , through air across an alveolus; and 3) $f(t)dt$, the probability of a tissue thickness, t , for an alveolar wall. If the particulate lies on the wall next to the site, the desired probability is $h(t)dt$; if on the next wall, it is $h(t)g(v)dt dv$; on the next, $g(v)dt dv$ times the convolution of h and f ; on the next, $dt dv$ times the convolutions of h and f and of g with itself; etc. The desired probability is the sum of the probabilities for all such possibilities. Term-by-term calculation, as described here, is straightforward but cumbersome; it takes a lot of computer time.

The actual calculation is made using transforms to effect the convolutions. Transforms also simplify the description of the calculation, because the convolutions required are given by the products of transforms. With capitals to denote transforms, the contributions just described are

$$H + HG + HFG + HFG^2 + \dots \quad (1)$$

It is possible to carry this series to more terms and then to show, formally, that it equals

$$\frac{H(1+G)}{1-GF} \quad (2)$$

I am now exploring the possibility of using this formal result to make the calculation instead of doing it term-by-term. Part of the difficulty in doing so is that H and F are transforms on one variable, t , while G is a transform on the other variable, v .

LUNG DOSE CALCULATIONS FOR BEAGLE DOGS EXPOSED TO $^{239}\text{PuO}_2$ --A PROGRESS REPORT

D. R. Fisher, W. C. Cannon and E. F. Blanton

The major emphasis of the Internal Microdosimetry program during recent years has been development of computer methods for determining specific energy densities in tissues surrounding alpha-emitting particulates. It was intended that these computational methods would be applied to practical problems in radiation biology.

One of the most important applications of internal microdosimetry involves a reassessment of specific energy distributions in lungs of beagle dogs that have participated in long-term plutonium dioxide ($^{239}\text{PuO}_2$) inhalation studies at Pacific Northwest Laboratory. After having demonstrated the initial capability to determine specific energy distributions for plutonium in a hypothetical dog lung (Fisher and Roesch 1981), we initiated work to characterize the microdosimetry of plutonium in actual dogs.

Several steps are required in the total development of this capability (Figure 1). Task 1 was essentially completed in 1977 (Roesch 1977), although further work was required for calculating the ionization frequency distributions in small sites (Wilson and Paretzke 1980). Task 2 was completed in 1981 with the development of a statistical description of dog lung microstructure (Fisher, Hadley and Roesch 1982). Task 3 has involved consolidating the lung model with the microdosimetry code for alpha-emitting particulates (as discussed in the next article), and has not been completed.

The lung microdosimetry code requires input information regarding the distribution, concentration, specific activity, and number of alpha-emitting particulates deposited in the lung. This requirement is complicated by the fact that $^{239}\text{PuO}_2$ aerosols inhaled by beagle dogs (as well as radiation workers in industrial accident situations) consist of a wide variety of sizes and shapes. Therefore, Task 4 involves describing the physical size and activity distribution of the

FIGURE 1. Priority and Progression of Tasks Involved in Characterizing the Microdosimetry of Plutonium in Beagle Dog Lungs

plutonium dioxide aerosols used in the previous experimental inhalation studies. Since many different plutonium aerosols were prepared at different times and with varying levels of activity, a separate aerosol characterization is required for each dog lung studied.

Original cascade impactor sampling data were used to reconstruct the plutonium aerosol size distributions for each of 60 different dogs. The plutonium aerosols were originally sampled and characterized in terms of their aerodynamic properties. Since our interest was also in the specific activity of plutonium in the aerosol particulates and since the specific activity is proportional to mass where the composition of particulates is homogeneous, we converted all aerodynamic size distribution data to physical size distribution data for each of the seven stages of the cascade impactor air sampler. A lognormal size distribution was assumed, and the conversion was made using the methods of Mercer (1973).

Task 5 involves the incorporation of lung deposition and retention parameters into the calculational model. Lung deposition is influenced by the aerodynamic properties of the aerosol inhaled and by the anatomical structure of the dog lung. The lung deposition model for the beagle dog (Yeh 1980), modified for high-density plutonium dioxide polydisperse aerosols, was adapted (Figure 2). Standard breathing rates for the beagle dog given by Yeh (1980) were assumed.

Lung retention of inhaled particles varies from one dog to another. The single long-term retention function ($T_{1/2}$) was determined for each dog from the formula

$$T_{1/2} = \frac{-t (\ln 2)}{\ln (LB_t/LB_0)} \quad (1)$$

FIGURE 2. Deposition Fractions for $^{239}\text{PuO}_2$ in the Pulmonary Region of Beagle Dog Lung: A Comparison of Experimental Data with Deposition Predicted by Theory (recalculated from data of Yeh 1980)

where $T_{1/2}$ is the time required for the lung burden to be reduced by one-half, t is the lifespan of the dog (days) following inhalation of plutonium, and LB_0 and LB_t are the plutonium lung burdens initially and at time of death, respectively. The mean $^{239}\text{PuO}_2$ residence half-time ($\pm$ S.E.) in lungs of 60 beagles was found to be 1115 ± 532 days. Individual values for each dog will be used in future microdosimetry calculations. The method for dealing with retention functions in microdosimetry calculations was presented in an earlier report (Fisher, Roesch and Harty 1982).

Task 6 involves calculation of the specific energy distributions for each of the 60 dogs. This work will enable comparison of the microdosimetry and observed biological outcome for each subject, and will lead to a better understanding of the correlations between dose distribution and biological effectiveness of inhaled plutonium in man.

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COMPUTER PROGRAM MODIFICATIONS FOR LUNG MICRODOSIMETRY

R. Harty and R. T. Hadley

Computer codes were previously developed at Pacific Northwest Laboratory to calculate the microdosimetry of internal alpha emitters present in the lung (Roesch 1981). These codes were created by revising the earlier microdosimetry codes that applied to homogeneous tissue to account for inhomogeneous lung tissues. A lung model based on statistical studies of beagle dog lung microstructure was incorporated to describe the distributions of tissue, air space, and cell nuclei in pulmonary lung tissue (Fisher and Roesch 1981).

The first lung microdosimetry codes were written in BASIC computer language for a desk top microcomputer. The codes were written to conserve memory and minimize run time. Even so, the calculations were time-consuming (10 h) and the program was inflexible due to memory capacity constraints. To alleviate this problem, the codes were translated into FORTRAN and loaded onto a larger computer. This work substantially shortened the time necessary for program execution (12-15 min) and increased the flexibility of the program.

Lung microdosimetry code revisions have required more effort than originally expected due to their complexity. We are currently in the process of documenting the code and verifying the FORTRAN code results using output from the original version written in BASIC. Important modifications being incorporated into the lung model include a revised statistical model of the dog lung (Fisher, Hadley and Bowen 1981) and a function to incorporate long-term migration and clearance of radioactive materials from the lung.

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SPECIAL WORKSHOP ON LUNG DOSIMETRY

D. R. Fisher

A Special Workshop on Lung Dosimetry was convened in Salt Lake City, Utah, on April 21-22, 1982, to stimulate the use of improved radiation dosimetry and to formulate a stronger basis for dose-response relationships for inhaled radionuclides. The two-day workshop was held in conjunction with the 30th Annual Meeting of the Radiation Research Society. The workshop

attracted a large number of participants from foreign countries in addition to the U.S. delegation.

Invited speakers at the workshop included Wolfgang Jacobi (West Germany), Joseph Diel and Bruce Boecker (Lovelace Foundation), Werner Hofmann (Austria), Darrell Fisher (Pacific Northwest Laboratory), and Paul Morrow (University of Rochester). The presentations centered on the adequacy of current models for lung dosimetry, the usefulness of microdosimetry, the value of data derived from animal studies, and the health impact of radon and its daughter products. Additional sessions of the workshop were devoted to retention and distribution of inhaled materials, and dose-response implications for man.

Radiation dosimetry of the lung is a complex subject because many variables are considered simultaneously. For example, lung clearance is the product of many competing processes: dissolution of particles, mechanical clearance by cilia, recoil or diffusion emanation of daughter products, and phagocytosis. New information was presented on long-term retention of inhaled particles in the upper respiratory tract of some experimental animals. If similar mechanisms are applicable to man, this finding could have significant health risk implications.

A frequent subject of discussion concerned inadequacies of the ICRP lung model (ICRP 1979) for estimating deposition and retention of internal emitters. Tables of retention and clearance values are given for different radionuclides, but for many industrial inhalation exposures the composition of the inhaled particle matrix is in fact more influential than the imbedded radionuclide. Also, current values for inhaled plutonium dioxide are inadequate for radiation dosimetry and health protection purposes.

New methods of track-etch alpha spectrometry were demonstrated that may be used to investigate both the spatial distribution and identity of mixed alpha emitters deposited in the respiratory tract.

At the microscopic level of dosimetry, the question of relevant dose was discussed at length. The inherent problems associated with conventional dose averaging and the stochastic nature of energy deposition by discrete alpha-emitting particles in the respiratory tract warrant continued microdosimetry studies. How the concept of "specific energy" can provide a better dose-response relationship is uncertain. The probability that a cell is traversed by an alpha particle may be a more important analytical tool than the specific energy it received in the process.

Further research is needed to determine the health significance of microscopic distributions of radiation energy in the lung from inhaled particulates of plutonium or other alpha emitters. Although the basic mechanisms of carcinogenesis are still largely unknown, improvements in dosimetry, such as those described at the workshop, will lead to a better understanding of the hazards associated with inhaled radioactive materials.

Publication of the full proceedings of the workshop is in progress.

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• Dosimetry of Internal Emitters

The Dosimetry of Internal Emitters program endeavors to refine the correlation between radiation dose and observed biological effects. The program is presently engaged in the development of studies that will demonstrate the applicability of microdosimetry models developed under the Microdosimetry in Internal Sources program. The program also provides guidance and assistance to the Biology and Chemistry Department of Pacific Northwest Laboratory in the dosimetric analysis of internally deposited radionuclides. The investigators work closely with the Biology and Chemistry Department staff and collaborate on the Microdosimetry of Internal Sources program.

CURIUM-LABELED POLYSTYRENE MICROSPHERE FOR MICRODOSIMETRY STUDIES

R. J. Traub and W. E. Skiens

We have prepared ^{244}Cm -labeled polystyrene microspheres for use in our microdosimetry studies. These microspheres have some specific advantages when compared with ceramic microspheres. First, the polystyrene microspheres have nearly unit density, thus corrections for self-attenuation in the particulate are simplified. Second, the unit density simplifies the mixture of these microspheres into biological media. Third, the activity associated with a microsphere may be readily altered without altering the size of the particulate.

The microspheres were prepared by complexing the ^{244}Cm with thenoyltrifluoroacetone. The Cm -thenoyltrifluoroacetone complex was separated from uncomplexed material by extraction into benzene. The benzene was evaporated from the metal complex and the residue metal complex was then dissolved in an equal volume of freshly distilled styrene monomer. An aqueous suspension of polymeric microspheres was then added to the ^{244}Cm -complex-styrene monomer solution. The entire solution was placed in a room temperature shaker for approximately five hours to allow the polymeric microspheres to become coated; following this, the entire solution was exposed to ~13 megarad of ^{60}Co radiation to polymerize the styrene monomer.

The microspheres were then washed to remove uncomplexed ^{244}Cm using repeated centrifugation and resuspension in water. This washing procedure was repeated until the wash solution contained negligible radioactivity. The labeled microspheres were suspended in a 0.04% lauryl sulfate solution to prevent clumping of the prepared microspheres.

Microspheres obtained to date have a nominal activity of 4 disintegrations per hour which is within the range of desired activity. We

intend to produce similar microspheres having activities of 40 disintegrations per hour.

MICRODOSIMETRY CELL STUDIES

R. J. Traub, M. E. Frazier and D. R. Fisher

Preliminary microdosimetry cell studies utilizing ^{239}Pu labeled ZrO_2 microspheres* were completed. The average alpha doses to the nuclei of the cells were calculated for a planar configuration using an internal microdosimetry computer code (Roesch 1977).

Chinese hamster ovary (CHO) cells were grown in flasks having a surface area of 25 cm^2 . Irradiation of the cells was performed by mixing the plutonium microspheres with the cells for a period of 7 h. There were two types of alpha irradiations: the first consisted of irradiating the cells by stationary microspheres, the second consisted of irradiating the cells by microspheres which were gently rocked among the cells to obtain a uniform alpha dose distribution. A third group of cells was irradiated in a gamma radiation facility.

The doses were calculated using the following assumptions.

1. Effective alpha energy = 4.3 MeV
2. Alphas emitted per sphere during the irradiation = 1744
3. Concentration of spheres on flask surface = 2.663×10^{-3} spheres/ μm^2
4. Cell nuclear diameter = $9\text{ }\mu\text{m}$

The calculated alpha absorbed dose to the system was 2440 rad.

The results of the experiment are shown in Table 1. The mutation rate for the alpha-irradiated cells that were shaken is ~4 times the mutation rate for the cells that were not shaken.

* Generously supplied by Dr. L. M. Holland, Los Alamos National Laboratory.

TABLE 1. Exposure of CHO Cells to Pu-ZrO₂ Microspheres *in vitro*

Group	Average Radiation Dose to Cell Nuclei	Additional Treatment	Mutants per 10 ⁶ Viable Cells
1	2442 rad α	—	6.8 $\pm$ 1.7
2	2442 rad α	gentle agitation	28.4 $\pm$ 4.0
3	66 rad γ	—	6.9
4	(Control)	—	1.5

Although more experimentation is planned, the preliminary results appear to agree well with the theoretical concepts of internal microdosimetry, and indicate the value of taking a closer look at dose distribution effects.

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