**Pacific Northwest Laboratory
Annual Report for 1976
to the
ERDA Assistant Administrator for
Environment and Safety**

**Part 4 Physical and Technological
Programs**

June 1977

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and Development Administration
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Programs**

**by
J. M. Nielsen and Staff Members
of Pacific Northwest Laboratory**

June 1977

**Battelle
Pacific Northwest Laboratories
Richland, Washington 99352**

PREFACE

Pacific Northwest Laboratory's 1976 Annual Report to the ERDA Assistant Administrator for Environment and Safety is organized by major program categories into five Volumes, or Parts. Parts 1-4 are oriented to particular segments of the program supported by the Division of Biomedical and Environmental Research. Part 5 includes reports on projects supported by the Division of Safety, Standards and Compliance; Division of Technology Overview; Division of Environmental Control Technology; and the Office of Environmental Policy Analysis. 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 1976 Annual Report are:

Part 1 Biomedical Sciences
Program Manager - W. R. Wiley	R. C. Thompson, Report Coordinator
D. L. Felton, Editor
Part 2 Ecological Sciences
Program Manager - B. E. Vaughan	B. E. Vaughan, Report Coordinator
J. L. Helbling, Editor
Part 3 Atmospheric Sciences
Program Manager - C. L. Simpson	J. M. Hales, Report Coordinator
E. L. Owzarski, Editor
Part 4 Physical and Technological Programs
Program Manager - J. M. Nielsen	J. M. Nielsen, Report Coordinator
G. M. Garnant, Editor
Part 5 Control Technology, Overview,
Safety, and Policy Analysis
Program Managers - N. E. Carter
D. B. Cearlock
J. C. Fox
D. L. Hessel
H. V. Larson	W. J. Bair, Report Coordinator
L. C. Counts/R. W. Baalman, Editors

Activities of the Environmental and Safety Research Program at PNL are broader in scope than the articles in this report indicate. PNL staff members participate throughout the year in many projects not funded through specific 189s. These efforts include overall program planning, response to requests for information from the ERDA Assistant Administrator for Environment and Safety and other officials, participation on national and international standard-setting committees, and public education. During 1976, staff of PNL's Environmental and Safety Research Program:

- prepared two volumes (Fission and Fusion) of ERDA's Balanced Program Plan for Biomedical and Environmental Research;
- contributed to a number of environmental assessments and impact statements, including the Generic Environmental Statement for Mixed Oxide Fuels and the Clinch River Breeder Reactor Statement, and participated in hearings on nuclear issues;
- sat on National Academy of Sciences/National Research Council Committees, the National Council on Radiation Protection and Measurements, and the International Commission on Radiological Protection;
- compiled and prepared the final reports for two of these committee efforts; and
- provided, in response to requests from the Assistant Administrator for Environment and Safety, interpretations of research results to clarify information given to the public on a number of issues. These included the Hanford Mortality Study findings, faulty published interpretations of data on mortality in plutonium workers, and several other issues concerned with nuclear power.

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

Previous Reports in this Series:

Annual Report for

1951	HW-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
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

FOREWORD

Part 4 of the Pacific Northwest Laboratories' Annual Report for 1976 to ERDA's Assistant Administrator for Environment and Safety includes those programs funded under the title Physical and Technological Programs. Reports on 189 program studies appear individually or grouped with related programs. Each section is introduced by a "blue page" which identifies the 189s reported on in that section.

This year's annual report covers ongoing physical and analytical research programs and new programs related to non-nuclear energy needs. Most of these new programs were first funded in 1976 and these initial reports emphasize overall planning and very early research results. New programs are progressing rapidly following planning, acquiring some necessary personnel and capital equipment, and establishing working relationships at operating fossil energy development centers. We would encourage your direct contact with our principal investigators for additional information beyond our brief progress reports contained herein.

To reflect redirection and growth in non-nuclear research, the name of the Radiological Sciences Department has been changed to the Physical Sciences Department. The department will continue basic studies of the chemistry and physics related to energy technologies, including reaction mechanisms and kinetics, analytical methods and instruments development, radiological physics, dosimetry and biophysics. Other activities that indicate the varied nature of the department's R&D are studies of earth, lunar and planetary composition and dynamic processes, environment and energy effluent characterization, transformation, and measurement, and the application of advanced ultrasensitive and selective analytical technologies.

CONTENTS

PREFACE	ii
FOREWORD	iv
PHYSICS AND CHEMISTRY OF POLLUTANT INTERACTIONS IN THE ENVIRONMENT	1
Reaction Kinetics of Combustion Processes	3
Chemical Kinetics - J. A. Campbell, R. D. Smith and J. C. Lau1	3
Methodology for Investigating Trace Metal Speciation on Flyash Particle Surfaces - W. C. Weimer and J. C. Kutt	6
References	7
RADIOLOGICAL AND CHEMICAL PHYSICS	9
Radiation Dosimetry and Radiation Biophysics	11
Temperature Effect on the Radiation Sensitivity and the Repair of Radiation Damage in <i>Chlamydomonas reinhardtii</i> - L. A. Braby and W. C. Roesch	11
Analysis of Methods for Determination of Mean Recovery Time Following Split-Dose or Protracted Irradiations - J. M. Nelson, L. A. Braby and W. C. Roesch	13
Experimental Methods for Use in Making Comparisons with Biophysical Models - L. A. Braby	13
Non-Equilibrium Microdosimetry - W. C. Roesch	14
Cell Cycle Modeling - W. C. Roesch	15
Dose Rate Models - W. C. Roesch	20
Dosimetry of Particulate Sources in the Lung	23
Calculations for Microdosimetry of Internal Sources - W. C. Roesch	23
Single-Event Probability Densities for Alpha Particles - W. E. Wilson	27
Experimental Microdosimetry for Alpha Particles - L. A. Braby and W. C. Roesch	28
Radiation Physics	30
Basic Collision Cross Sections	30
Energy Dependence and Inner Shell Effects in Differential Ionization Cross Sections for Fast Protons - L. H. Toburen and S. T. Manson	30
Energy and Angular Distributions of Electrons Ejected from Water Vapor by 0.3-1.5 MeV Protons - L. H. Toburen and W. E. Wilson	33
Differential Ionization of Noble Gases and Water Vapor by Helium Ions and Alpha Particles - L. H. Toburen, R. J. Popowich and W. E. Wilson	34
Potential Barrier Effects in the Ionization of Symmetric Molecules - L. H. Toburen and W. E. Wilson	37
Ionization by Protons: 5 to 50 keV - T. L. Criswell and L. H. Toburen	37
Molecular Effects in Inner Shell Ionization - L. H. Toburen, D. J. Lynch, R. P. Chaturvedi and W. E. Wilson	39

Analytical Expression for Cross Section Data - W. E. Wilson	40
Radioluminescence Studies	43
Experimental Radioluminescence Studies - M. L. West and J. H. Miller	43
Fluorescence Quenching Model - J. H. Miller and M. L. West	45
References	48
Publications and Presentations	51
CHARACTERIZATION, MEASUREMENT, AND MONITORING	53
Radiation Instrumentation--Radiological Chemistry	55
High Sensitivity Isotope Analysis with a ^{252}Cf - ^{235}U Fueled Subcritical Multiplier and Low Background Photon Detector System - N. A. Wogman, H. G. Rieck, J. C. Laul and K. W. MacMurdo	55
Transuranium Element Measurement Techniques for High and Low Level Wastes Associated with Power Reactor Fuels Processes - N. A. Wogman	58
Use of X-Ray Spectrometry in Neutron Activation Analysis - K. K. Nielson, J. C. Laul and N. A. Wogman	59
In-Situ Activation and Photon Detection Techniques for Uranium Ore Evaluation - R. L. Brodzinski and N. A. Wogman	60
Environmental Pollution Analysis - Instruments and Methods Development	62
Analysis of Trace Elements in Sea Water by Anodic Stripping Voltammetry (ASV) - K. H. Abel and E. A. Crecelius	62
Analysis of Mercury Species in Water - C. L. Wilkerson and E. A. Crecelius	62
Analysis of Arsenic, Antimony and Selenium in Solution by X-Ray Fluorescence of Ferric Precipitate - E. A. Crecelius	63
Matrix Corrections for X-Ray Fluorescence Analysis Using Scattered X-Rays - K. K. Nielson	63
Evaluation of a Simple Method for X-Ray Peak Analysis - K. K. Nielson	64
Oil Shale and Tar Sand Research	66
Gas Chromatography/Mass Spectrographic Analysis of Shale Oil Fractions - P. W. Ryan	66
Characterization of Products, Effluents and Wastes from Oil Shale Retort Pilot Plants - J. S. Fruchter, M. R. Petersen and J. C. Laul	67
Fossil Fuel Research Materials: Preparation and Documentation - J. S. Fruchter and M. R. Petersen	71
Determination of Mercury in Coal and Oil Shale Materials - C. L. Wilkerson	72
Multielement Analysis by Sequential Instrumental Neutron Activation - J. C. Laul, L. A. Rancitelli and J. S. Fruchter	74
Analysis of Coal Conversion and Oil Shale Retorting Materials by Radiochemical Neutron Activation Analysis - J. C. Laul and J. S. Fruchter	76
Measurement of Toxic Materials in Geothermal Fluids - J. S. Fruchter, D. E. Robertson and J. D. Ludwick	79

Dosimetry of Internal Emitters	83
Dose to G.I. Tract from Ingested Insoluble Beta Emitters - F. T. Cross and G. W. R. Endres	83
Analytical Techniques for ^{99}Tc Measurement in Environmental Samples	85
Ultrasensitive Measurement of ^{99}Tc by Mass Spectrometry - J. H. Kaye	85
Trace Constituent Analysis by Laser Excitation	88
Analysis of Trace Constituents by Laser Excitation - B. A. Bushaw and T. J. Whitaker	88
Application of Holography	92
Application of Holography to Environmental Studies - B. P. Hildebrand	92
Real-Time Measurement of Plutonium in Air at Below MPC Levels	95
Direct-Inlet Mass Spectrometer Development - J. J. Stoffels and C. R. Lagergren	95
References	97
Publications and Presentations	98
PUBLICATIONS AND PRESENTATIONS	101
ORGANIZATION CHARTS	107

PHYSICS AND CHEMISTRY OF POLLUTANT INTERACTIONS IN THE ENVIRONMENT

- **REACTION KINETICS OF COMBUSTION PROCESSES**

-
- **BULLET DENOTES 189 TITLE**

• REACTION KINETICS OF COMBUSTION PROCESSES

The goal of the Reaction Kinetics of Combustion Processes program is the development of a model which will predict the chemical and physical forms of the gas and particulate emissions at any point past the combustion source, and to predict the chemical reactions which occur before meteorological and diffusional considerations dominate. Fly ash has been characterized by electron spectroscopy for chemical analysis (ESCA), x-ray fluorescence and neutron activation. These studies suggest the concept of trace element differentiation, with certain trace elements being more concentrated at the surface than within the particulate. Since the chemical state of the trace element will often determine its environmental availability and toxicity, a methodology is being developed which can identify sub ppm levels of several valence states of 12 potentially toxic trace elements.

Chemical Kinetics

J. A. Campbell, R. D. Smith and J. C. Lau

The complex physical and chemical processes which occur in coal combustion must be better understood to determine their health and environmental impact. Better understanding of the chemical events following combustion is also mandatory to improve pollution control devices and to develop a firm base for regulatory action. The goal of the Chemical Kinetics program is the development of a model based on primary rate data which will predict the chemical and physical forms of the gas and particulate components at any given point past the combustion source.

The initial approach to this problem has been threefold: 1) a mathematical model using existing rate data is being assembled for comparison with laboratory or field results as they become available; 2) flyash has been chemically and physically characterized with emphasis on its trace element composition; and 3) laboratory experiments are being developed to probe the gas phase and gas-solid processes which occur following combustion.

The origin and the composition of flyash generated in coal combustion, to a first approximation, may be explained in terms of the following model: assume that finely pulverized coal is injected into the firebox. The carbon and hydrogen components are instantly oxidized; other components including trace elements may be volatilized. Non-volatile microparticulates can then serve as nucleation centers for the condensation of the volatilized materials. This condensation probably occurs in a layered ordering, i.e., an "onion skin" configuration with the highest boiling materials condensing first, followed by consecutive condensation of the remaining lower boiling components as a function of cool down temperatures. This can be seen in schematic form in Figure 1.1. Some materials that remain volatile at low temperatures will escape from the stack. Particles in the sub-micron region may also escape the precipitators and be released with the plume.

In order to gain a better understanding of the flyash surface and to evaluate the "onion skin" theory, physical and chemical examinations of these surfaces were undertaken. Electron spectroscopy for chemical

FIGURE 1.1. Schematic Diagram Depicting the "Onion Skin" Model for Condensation of Various Vapor Phase Species on Flyash. Boiling Point A > Boiling Point B > Boiling Point C.

analysis (ESCA) was applied to determine the major surface constituents, and their oxidation states. These were found to be primarily O, Si, Fe, Al, Ca, Na, C, and S. Approximately 50 Å of the surface layer was then removed by sputtering. Electron spectroscopy of the newly exposed area showed higher concentrations of Al, Fe and Si than the respective concentrations on the surface. Conversely, Ca, C, Na, and S were found to decrease with depth, shown pictorially in Figure 1.2. These results lend support to the hypothesis of condensation layering of more volatile components on a matrix of oxides of silicon and aluminum. From x-ray diffraction power patterns, the matrix is considered to be primarily SiO_2

and Al_2SiO_5 . These results are also supported by the recent work of Natusch, et al.¹ who examined flyash under a different analytical protocol.

Heating experiments were used to determine the reverse order in which gaseous constituents were condensed on the flyash. The reverse order will be dependent upon the nature of surface bonding and neglects the possibility of diffusion between layers. Since the amount of material removed is small compared to the matrix of the flyash, neutron activation, a very sensitive technique for trace metal analyses, was used to measure the loss of volatiles. After radioactively cooling for 2 days following

FIGURE 1.2. Simplified Pictorial Representation of Results Obtained in ESCA Studies of Flyash. A = C, S, Na, and Ca; B = Al, Fe, and Si.

activation, 100-200 mg samples were placed in a Pt crucible within a specially designed furnace and held at a specified temperature for approximately 2 1/2 hr. Volatile materials were collected on charcoal and counted for gamma activity in a low background, high efficiency detector system. At the four temperatures used, between 550 and 1100 C, the collection rate for all elements increased with temperature. The elements detected were Hg, Br, As, Zn, Sb, Se, Na, K, and Cs. The elements Se, Sb, and Hg were found to volatilize at 500°C with an increase in concentration obtained at 1000°C for each element, probably indicating the presence of two chemical forms for each element.

To further explore these complex chemical systems, significant effort has been devoted to the construction of two laboratory experiments for the characterization of coal combustion processes. These experiments are designed to allow manipulation of the macroscopic parameters (fuel/oxygen ration, fuel composition, flow rates, concentration of particulate matter, etc) to provide the necessary input for successful modeling. The first apparatus, shown in Figure 1.3, is a flow tube with a movable combustion region

which will be used to simulate the combustion region and stack of coal-fired plant. Combustion occurs in the furnace at any desired distance (up to 14 ft) from the sampling cone. At the sampling cone, gaseous species moving through the orifice, form a collimated molecular beam which is mechanically chopped, ionized, and detected using a quadrupole mass spectrometer. Phase sensitive detection, using a lock-in amplifier, assures that only molecular beam components are detected.

A second instrument, also under construction, is a high temperature furnace (up to 3000°C) from which species may be sampled and studied using the same mass spectrometer described above. The furnace will be equipped with a Knudsen type cell or other high temperature reactor configurations. Gas inlet control is provided to allow study of specific gas-solid reactions at selected temperatures. The combination of these two experiments should provide adequate experimental input for further sophistication of the mathematical model.

FIGURE 1.3. Modulated Beam Mass Spectrometer with Flow Tube Combustion Reactor

Methodology for Investigating Trace Metal Speciation on Flyash Particle Surfaces

W. C. Weimer and J. C. Kutt

The concentration of several toxic trace metals that are attached to the surface of flyash particles is too low to be quantified by instrumental techniques. A chemical leaching methodology is proposed which can identify and quantify sub-ppm levels of several valence states of 12 potentially toxic trace metals. This method enhances the ability to predict the fates of such toxic trace metals associated with coal combustion byproducts.

The determination of the chemical species and concentrations of trace elements on the surface of flyash particles is essential to model the interaction of effluents during the coal combustion process and to predict the fates and effects of the release of these elements into the environment. Instrumental techniques available for surface analyses are not sufficiently sensitive to measure most trace elements on the surface of flyash particles. These techniques generally permit quantification for only those elements which have surface concentrations of parts per thousand or greater. Alternatively, a chemical desorption solution with a redox potential approximately equal to that of natural water can be used to remove surface-associated trace metals from flyash particles. The chemical solutions used are hard acids with a high charge-to-radius ratio. A solution such as LaCl_3 will remove chemical species of metals held to flyash surfaces by weakly cohesive attachments such as van der Waal's forces, specific adsorption, or reversible ion exchange processes. After a solid-solution contact period, concentrations of chemical species of the metals of interest are determined in the desorbing solution. In theory, it is possible to

remove essentially all surface-associated trace metals by this desorption technique without a concomitant dissolution of the particle matrix and without altering the chemical state of the trace elements.

The trace elements that may be examined by this approach include As, Hg, Sb, Se, Ni, Cr, Cu, Cd, Pb, Zn, V, and Sn. A combination of several different analytical procedures are used to determine the concentrations of these trace metals in flyash leaching solutions. These techniques include flameless atomic absorption spectrometry, direct current discharge emission spectrometry, and several electrochemical techniques--differential pulse polarography, differential pulse cathodic stripping voltammetry, and differential pulse anodic stripping voltammetry. The detection limits for these techniques for trace metals in solution are listed in Table 1.1, together with the forms of the trace elements which are quantified. Controlled oxidation or reduction steps in conjunction with these instrumental measurements permit the identification and quantification of the species of these metals which are listed in Table 1.2.

This approach to the determination of the chemical states and concentrations of trace metals attached to the surface of flyash particles is more sensitive for most trace elements than any other instrumental technique available today. The determination of the chemical species of trace metals on flyash particle surfaces will greatly enhance the ability to predict the environmental fates and effects of trace elements associated with byproducts of coal combustion. In addition, these speciation studies will lead to an improved basic understanding of the interaction of trace elements with other products and effluents during the coal combustion process.

TABLE 1.1. Sensitivities of Elemental Analyses

ELEMENT	LIMIT OF DETECTION--NG	FORM QUANTIFIED	TECHNIQUE*
Hg	0.01	Hg ⁰	FFA
Se	0.5	Se ⁺⁴	DPCSV
Zn	0.5	Zn ⁺²	DPASV
Cd	0.5	Cd ⁺²	DPASV
Pb	1.0	Pb ⁺²	DPASV
As	1.0	AsH ₃	DCE
Sb	1.0	SbH ₃	DCE
Cu	10.0	Cu ⁺²	DPASV
Ni	100.0	Ni ⁺²	DPP
Cr	120.0	Cr ⁺⁶	DPP
V	400.0	VO(SCN) ⁺	DPP
Sn	800.0	Sn ⁺⁴	DPASV

*FAA - FLAMELESS ATOMIC ABSORPTION SPECTROMETRY
 DPCSV - DIFFERENTIAL PULSE CATHODIC STRIPPING VOLTAMMETRY
 DPASV - DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY
 DCE - DIRECT CURRENT DISCHARGE EMISSION SPECTROMETRY
 DPP - DIFFERENTIAL PULSE POLAROGRAPHY

TABLE 1.2. Identifiable Metal Species

Hg ⁰	Pb ⁺²	Ni ⁺²
Hg ⁺²	As ⁺³	Cr ⁺³
HgCH ₃ ⁺	As ⁺⁵	Cr ⁺⁶
Hg(CH ₃) ₂	CH ₃ AsH ₂	V ⁺³
Se ⁰	(CH ₃) ₂ AsH	V ⁺⁴
Se ⁺⁴	Sb ⁺³	V ⁺⁵
Se ⁺⁶	Sb ⁺⁵	Sn ⁺²
Zn ⁺²	Cu ⁺²	Sn ⁺⁴
Cd ⁺²		

REFERENCE

1. R. W. Linton, A. Loh, D. F. S. Natusch, C.A. Evans, Jr., P. Williams, "Surface Predominance of Trace Metals in Airborne Particles," Science 191, p. 852, 1976.

RADIOLOGICAL AND CHEMICAL PHYSICS

- **RADIATION DOSIMETRY AND RADIATION BIOPHYSICS**
- **DOSIMETRY OF PARTICULATE SOURCES IN THE LUNG**
- **RADIATION PHYSICS**
 - **BASIC COLLISION CROSS SECTIONS**
 - **RADIOLUMINESCENCE STUDIES**

• RADIATION DOSIMETRY AND RADIATION BIOPHYSICS

The joint purpose of these two closely integrated programs is to explore the connections between the primary physical events produced by radiation and their biological consequences in cellular systems. The radiation dosimetry program includes theoretical description of the primary events and their connection with the observable effects and experimental realization and measurement of the physical parameters needed by the theory. The radiation biophysics program tests or makes use of the theoretical developments and gathers information needed for the theories by experiments on cellular systems. This year measurement of the temperature variation of the parameters for the fraction of cells surviving irradiation led to identification of an enzymatic recovery process and a competitive process for radiosensitivity. A mechanically controlled microscope with a wide viewer and recorder was assembled to permit precision survival measurements at low doses. A study of the microdosimetry of radiation nonequilibrium for neutrons showed the departures from equilibrium were small. As part of work on modeling the changes in radiation sensitivity during the cell cycle a simple, but exactly solvable, model of the cycle was developed to serve as a test system for more complicated, but approximate, models. Analysis of a number of models for the effects of the dose rate on cells showed that all but one of them could be eliminated by our experiments on *Chlamydomonas reinhardi* last year.

Temperature Effect on the Radiation Sensitivity and the Repair of Radiation Damage in *Chlamydomonas reinhardi* L. A. Braby and W. C. Roesch

Temperature has long been known to affect the survival of irradiated cells; but whether this is an effect on the probability of producing damage or an effect on the recovery process, or both, is not known. We re-examined data in the literature to this end but were unable to reach any firm conclusions. Therefore, we resumed our study of *Chlamydomonas reinhardi*, an organism in which we have been able to measure the damage and recovery processes separately,¹ and are now measuring them over a wide temperature range. While the measurements are not yet complete, we can safely conclude that both

processes are affected by temperature but in quite different ways. The recovery appears to be a typical enzymatic process, while the production of damage appears to be an inhibited (or competitive) process.

C. reinhardi was grown and exposed as before.¹ The two-event factor (A) and the mean recovery time (τ) were determined from our theoretical analysis² of split-dose experiments, which gave

$$\ln (S_m/S) = A D_1 D_2 \exp(-t/\tau) \quad (1)$$

for the fraction (S) surviving two doses (D_1, D_2) delivered a time t apart. S_m is the product of the fractions surviving the single doses D_1 and D_2 . All cells examined at a given temperature on a given day were put in

a temperature-controlled box 1/2 hr before any of them were exposed. About 15 min were required to reach the desired temperature. All cells were kept at the given temperature until 1 hr after the last group was exposed. The dose rate was nominally 5 krad/min and two equal doses of 5.35 krad were used. S_m was determined from 5.35 krad exposures given at the beginning and the end of measurements at a given temperature; these results generally were equal within the counting statistics. The surviving fraction was determined by counting both live and dead cells with the video system described elsewhere in this report.

Figure 2.1 shows the results of two typical experiments. The logarithm of $\ln(S_m/S)$ is plotted versus t , because Eq. (1) indicates the data should fall on a straight line whose intercept is AD_1D_2 and whose slope is τ^{-1} . The data do appear to be reasonably well fitted by straight lines.

The mean recovery times given by the slopes in Figure 2.1 differ substantially. The mean recovery times measured so far are given in Figure 2.2 as an Arrhenius plot: logarithm of the reaction rate (the inverse of the recovery time) versus the inverse of the absolute temperature (T). No curve is drawn between the points yet, because several measurements remain to be made. But the curve will clearly have the shape typical of enzymatic reactions: an increasing rate as the temperature is at first increased, followed by a decreasing rate due to enzyme denaturation. The optimum temperature is between 20° and 25°C., which is consistent with the temperatures in *C. reinhardi*'s natural environment.

FIGURE 2.1. Results of Split-Dose Experiments with *C. reinhardi* at Different Temperatures

FIGURE 2.2. Arrhenius Plot for the Mean Recovery Time of *C. reinhardi*

The two-event factors given by the intercepts in Figure 2.1 differ only slightly; however, the Arrhenius plot in Figure 2.3 of all the factors measured so far shows that the two-event factor decreases with increasing temperature. The two-event factor is not a reaction rate; it is a measure of a final reaction product (cell death). The decrease with increasing temperature suggests that cell death is in competition with other reactions and that these others become relatively more probable with increasing temperature. A simple model based on this concept predicts that the Arrhenius-type plot should be linear -- as it is observed to be in Figure 2.3.

The principal results of these measurements is their evidence for the enzymatic and competitive nature of the reactions involved. In addition, when the measurements are complete, activation energies will be derived from the Arrhenius plots for comparison with similar data for other cells.

FIGURE 2.3. Arrhenius Plot for the Two-Event Factor of *C. reinhardi*.

Analysis of Methods for Determination of Mean Recovery Time Following Split-Dose or Protracted Irradiations

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

With some additional work, the measurements noted in the preceding article are being used to study another matter. Laurie, et al.,³ following a suggestion by E. L. Powers, hypothesized that a pool or pools of material used in the repair process might exist in the cell. They deduced that recovery times determined in protraction and split-dose experiments might differ -- one reflecting the rate of using the pool, the other the rate of refilling it. The existence of these pools has not been demonstrated. Our experiments of the two types^{4,5} showed no sign of two recovery times, but unnoticed changes in temperature may have hidden a difference. The existence of such a pool phenomenon would, of course, be important to the model we are working on. Consequently, we are adding protraction experiments at a few temperatures to the work described above so we may compare recovery times from protracted exposure with those determined by the split-dose method. So far the recovery times determined by the two methods have not differed significantly. We expect to conclude that they do not differ and, therefore, give no evidence of a pool effect.

The protraction experiments used *Chlamydomonas reinhardi* grown, exposed, and temperature-controlled as described above. One survival curve is obtained at 25-50 rad/min and another at about 5,000 rad/min. These are analyzed to obtain the mean recovery time by the method in Ref. 5.

Experimental Methods for Use in Making Comparisons with Biophysical Models

L. A. Braby

A primary goal of the radiation dosimetry and biophysics programs is to develop and test mathematical models of radiation effects which will be applicable at the low doses and dose rates encountered in the environment. A major aspect of this is investigation of the "shoulder" region of the normal proliferative survival curve. This means measuring the survival at high surviving fractions, frequently above 90%, with precision adequate to detect deviations from the theoretically predicted behavior. In order to determine 90% survival to $\pm 3\%$ (relative standard deviation) by the conventional technique of plating a measured amount of known cell suspension, approximately 1,000 colonies would have to be

counted. However, if the exact number of cells at risk were known, only 90 need be counted. Thus, a number of valuable experiments which would not otherwise be practical can be carried out if the fate of individual cells is determined after irradiation. Observation of individual cells also gives additional information. Answers to the following questions are now possible: How many divisions were completed before division ceased? Was division normal? Were giant cells produced? Is the relative frequency of the recognizable forms of death dependent on the radiation type, dose rate, or environmental factors?

Depending on the type of cell being irradiated, some or all of this information can be obtained by various techniques. For many experiments involving long exposure times, *Chlamydomonas reinhardi* is a convenient species because it has a long period of nearly constant radiation sensitivity and normally divides synchronously when grown in a regular light-dark cycle. *C. reinhardi* also lends itself to counting the number of cells at risk because colonies will grow as round monolayer disks on minimal media agar when covered with a thin layer of silicone oil. Also, the cell wall remains clearly visible for days after the cell has ceased to grow and/or has lost its color. Thus, both the number of growing colonies and the number of cells that ceased to grow as single cells or small colonies can be easily counted by observation with a moderate power microscope.

In order to reduce operator fatigue and improve efficiency, the microscope has been replaced by a television camera and monitor with a net magnification of approximately 100. The microscope stage has been connected to a stepping motor with raster advance, focus, and counting registers controlled from a small keyboard. This makes a system which allows scoring a large number of cells as live or dead in a relatively short time.

This simple system will not work for mammalian cells because they disintegrate soon after death and those which did not survive cannot be located at the same time survivors can be identified. Counting surviving mammalian cells is further complicated by the tendency of mammalian cells to float loose of a colony and start a new one elsewhere. Both the problem of locating non-surviving colonies and the chance colonies due to floaters can be solved by providing stop frame video recording of images on a stationary stage microscope as illustrated in Figure 2.4. Furthermore, this system

FIGURE 2.4. Schematic Illustration of Multiple Plate Video Recording (VTR) System

allows one to follow the ways in which cells die by recording the image of each cell at various times during incubation.

Since it is highly desirable to test various aspects of radiation effects models on various cell systems including mammalian cells, an apparatus to scan dishes and record images of mammalian cells is being developed. Our experience with a hard-wired controller used to scan dishes of *C. reinhardtii* indicated that a mini-computer based system was desirable to allow simple modification of the scanning program to cover various combinations of one or more dishes and provide a set of registers for counting cells and recording identification numbers. Video tape will be used to record the image at given addresses of the scanning system and the address information will be enclosed in machine readable form along the edge of the video frame, thus allowing quick recall of images for time resolved comparison.

The system is illustrated schematically in Figure 2.4. The scanning system is completed and the optical system has been tested separately. Control circuitry to

properly position the tape in freeze frame video playback is being developed. The anticipated operating mode will allow scanning of several dishes in a stage incubator at a preset interval and (by re-winding the tape between scans) records of images as successive frames will provide easy access for viewing the time evolution of a colony, i.e., the tape will contain the time-lapse histories of each cell in the scanned area.

Non-Equilibrium Microdosimetry W. C. Roesch

Last year we began to develop methods for calculating microdosimetric distributions for internally deposited alpha-particle emitters, in particular, to investigate questions about the spatial distribution of dose around particulates. Progress this year is reviewed under the Dosimetry of Particulate Sources in the Lung program in this report. Part of that progress was the development of fast computer programs that can calculate microdosimetric distributions for general distributions of emitters in soft tissue. The theory and methods developed for that

study can also be used to shed light on certain basic problems in the microdosimetry of external radiations. In particular, they can be used to study the microdosimetry of locations where radiation equilibrium does not exist -- something that previous techniques could not do. A pilot study of the microdosimetry of radiation non-equilibrium was made with the internal microdosimetry computer programs. Because of the limited information available, a hypothetical radiation had to be used for this purpose, but it sufficed to display the effects of the non-equilibrium and to permit the conclusion that (at least for high-LET radiations such as those from neutrons) the effects are of no particular concern.

The Fourier transform (F) of the probability density in specific energy [$f(z)$] for external radiation is

$$\underline{F}\{f(z)\} = \exp[-\int_0^\infty \mu \Omega (1 - \underline{F}\{f(z;r,1)\}) dV] \quad (1)$$

where $f(z;r,1)$ is the single-event density due to charged-particle secondaries emitted in the volume element dV at distance r from the site, Φ is fluence of the external radiation, μ is its attenuation coefficient, and Ω is the probability that a secondary emitted from dV will affect the site.

This formula was applied to the study of an external radiation not too far from equilibrium. As done earlier for ordinary dosimetry,⁶ the fluence was approximated by $\Phi = \Phi_0 e^{\mu x} = \Phi_0 (1 + \mu x)$, where x is distance measured along the primary beam but opposite to its direction. Then,

$$\begin{aligned} \underline{F}\{f(z)\} = & \exp[-\Phi_0 \mu \int \Omega (1 - \underline{F}\{f(z;r,1)\}) dV] \\ & * \exp[-\Phi_0 \mu^2 \int x \mu (1 - \underline{F}\{xf(z;r,1)\}) dV] \end{aligned} \quad (2)$$

The right-hand side of this equation is a product of two transforms whose inverses can be calculated with the fast, internal-microdosimetry computer programs. The final distribution is then obtained by convoluting these two results.

The only $f(z;r,1)$ -densities and Ω -probabilities now available are the approximate ones being used in the internal microdosimetry work with alpha particles.⁷ For the present study, a hypothetical radiation

was used that employs these data. The secondaries were 5.15 MeV alpha particles emitted isotropically into the forward hemisphere. The track structure for alpha particles is similar to that for protons of one-fourth their energy; thus, the present results are an approximation to those for neutrons of about 1 MeV.

The size of the non-equilibrium effect depends on the relative values of μ and the average range of the secondary particles. Realistic values of these parameters led to changes in the density in specific energy too small to be seen when plotted.

To understand better what the changes were, even though they were negligible, the size of the argument in the second factor on the right of Eq. (2) are arbitrarily increased by a factor of ten and the calculation repeated. Figure 2.5 shows the result in a case when the absorbed dose was low enough that a significant fraction (64%) of the sites were not struck by any charged particle. The dashed line is the density in specific energy calculated as though radiation equilibrium existed; the solid line is that calculated for non-equilibrium from Eq. (2). There is generally an increase in density at all specific energy. This is a characteristic of all changes in probability density when the no-event probability is large;⁸ on the other hand, when the no-event probability is small, densities change by shifting to higher specific energy. This is illustrated in the present study by Figure 2.6, which is similar to Figure 2.5 but for a dose large enough that less than 2% of the sites were not hit. Both the equilibrium and non-equilibrium densities are nearly normal distributions at this high dose; hence, when the density shifts to higher specific energy, it decreases in height and increases in width.

This pilot study confirms the conclusion of ordinary dosimetry:⁶ for neutrons, the effect of non-equilibrium (outside secondary-particle transition zones) is small. Further, it shows that what changes there are in the density in specific energy are of familiar kinds.

Cell Cycle Modeling W. C. Roesch

Modeling the changes in cellular response during the cell cycle requires making choices among the many methods in the literature for modeling the events in the cycle and the

FIGURE 2.5. Density in Specific Energy for Equilibrium (dashed line) and Non-equilibrium (solid line) at a Low Dose for an Hypothetical Radiation Similar to 1-MeV Neutrons--the Difference Between the Curves Is Exaggerated as Described in the Text

FIGURE 2.6. Same as Figure 2.1, but for a High Dose

status of the cell's biochemical pathways. These methods were developed independently and the relations between them are unclear. A simple, n-state, cyclic model gives a convenient way of relating the methods, because an exact solution to the model can be found and the approximate solutions by the different methods can be compared to it to estimate their accuracy.

The n-state, cyclic model is given by the differential equations:

$$\begin{aligned} dp_1/dt &= -k_1 p_1 + q k_n p_n \\ dp_i/dt &= -k_i p_i + k_{i-1} p_{i-1}, \quad i = 2, \dots, n \end{aligned} \quad (1)$$

and is illustrated in Figure 2.7. The p_i are the populations of the states, and the k_i are their rate constants. For each member of the population leaving state n , q members re-enter state 1. The Laplace transforms, L_i , of the populations are conveniently given in terms of the two functions:

$$A(i,s) = \frac{k_1 k_2 \dots k_i}{(s + k_1)(s + k_2) \dots (s + k_i)} \quad (2.a)$$

$$B(i,s) = -d(\ln(A(i,s)))/ds = \sum_{m=1}^i (s + k_m)^{-1} \quad (2.b)$$

where s is the transform variable. The solution for the initial condition in which the whole population is in state 1 is:

$$k_1 L_i = A(i,s)/(1 - q A(n,s)) \quad (3.a)$$

$$= A(i,s) \sum_{m=0}^{\infty} (q A(n,s))^m \quad (3.b)$$

This transform can be inverted, at least in principle, by expanding each term in the series in partial fractions.

Each term in the series is an A-function or a product of several of them. In either case, the term is a product of factors each of which is itself a Laplace transform. This means that the inverse is the multiple convolution of the inverses of the factors in the product. The mean of the result of a convolution equals the sum of the means of the convoluted functions, and its variance equals the sum of their variances. In the n-state model, the inverses of the factors are exponential function. The mean of an exponential function is the inverse of its rate constant, and its variance is the inverse of the square of its rate constant. Thus, the terms in the series solution represent successive passages through the states at mean times $t_i + t_n$, where

$$t_i = \sum_{m=1}^i k_m^{-1} \quad (4)$$

The successive waves have increasingly large variances, $\sigma_i^2 + m \sigma_n^2$, where

$$\sigma_i^2 = \sum_{m=1}^i k_m^{-2} \quad (5)$$

i.e., the population becomes desynchronized. Figure 2.8 shows a few of the early waves in a 24-state, equal- k (see below), cyclic model.

The increasing desynchronization spreads the population through the states. Eventually the population reaches a stationary distribution; and the total number, and the number in each state, increases (if $q > 1$; decreases, if $q < 1$; stays the same, if $q = 1$) exponentially with time. Then,

$$k_i p_i = (A(i,w)/B(i,w)) e^{wt} \quad (6)$$

where w is found by solving

$$q A(n,w) = 1 \quad (7)$$

The approximate solution to this equation is

$$w = \ln(q)/t_n \quad (8)$$

FIGURE 2.7. The N-State, Cyclic Model

FIGURE 2.8. The Populations in the States of a 24-State, Cyclic Model at Times 0.1, 0.5, and 1.0 Times the Mean Transit Time Through the System. The whole population was initially in state 1. $q = 2$.

which says, for $q = 2$, that the doubling time is approximately equal to the mean transit time through the model. In the stationary distribution, the fraction of the population in each state is

$$q w A(i, w) / (k_i (q - 1)) \quad (9)$$

The solution to the model for more general initial conditions--populations p_{m0} in the states--is

$$k_i L_i = (A(i, s) / (1 - qA(n, s))) \left(\sum_{m=1}^i p_{m0} / A(m-1, s) + qA(n, s) \sum_{m=i+1}^n p_{m0} / A(m-1, s) \right) \quad (10)$$

where $A(0, s) = 1$. If the p_{m0} equal the fractions, Eq. (9), of the stationary distribution, Eq. (10) can be summed and gives the stationary, exponentially increasing solution, proportional to Eq. (6), again. In other words, if the model is started in its stationary distribution, it stays in that distribution and all populations increase exponentially. If started with any other p_{m0} 's, the model will go through

transients but will finally stabilize into exponential growth with the relative populations given by Eq. (9). Suitable choices of the p_{m0} make it possible to model labeling experiments and the effects of transient perturbations. The effects of drugs, or other treatments that alter the rate constants, can be modeled by suitably changing the k 's.

Models are also needed for the mitotic selection technique¹ in which cells are permitted to reach the exponential phase of growth and then are collected and counted as they reach mitosis. The technique is modeled by eliminating the return from state n to state 1 and defining the yield (y) as the rate of exit from state n , i.e., $y = k_n p_n$. The transform of the yield is:

$$Y = A(n, s) \sum_{m=1}^n p_{m0} / A(m-1, s) \quad (11)$$

For the control cultures, the p_{m0} are the fractions, Eq. (9), for the stationary phase and

$$Y = (w / (q - 1)) (1 - q A(n, s)) / (s - w) \quad (12)$$

The various modeling methods in the literature can now be fitted into the conceptual framework of the n -state, cyclic model simply by giving the A -function for the method. Space permits only a brief sketch of some of the possibilities.

When n is not too large--say less than a few hundred--a convenient approximation is obtained by replacing each of the k_i with a single, mean rate constant (k) defined by

$$k^{-1} = t_n / n = (1/n) \sum_{m=1}^n k_m^{-1} \quad (13)$$

Then,

$$A(i, s) = (k / (s + k))^i \quad (14)$$

Products of A 's are just higher powers of the ratio $k / (s + k)$. The inverses are gamma distributions

$$k (kt)^{i-1} e^{-kt} / (i-1)! \quad (15)$$

and the approximate solutions to the model can be built up from these distributions. Figure 2.9 illustrates the quality of the approximation for the first passage through the fourth state in an n -state model. Also, Figure 2.8 was calculated with this equal- k approximation.

FIGURE 2.9. The First Wave Through the Fourth State of an N-State Model. $k_1 = 1$, $k_2 = 1/2$, $k_3 = 1/3$, $k_4 = 1/4$. The solid line is the exact calculation, Eq. (2); the dotted line is the equal- k ($k = 0.4$) approximation, Eq. (15).

Another approximation is based on the fact that the result of repeated convolutions approaches the shape of a normal distribution, regardless of the shapes of the functions that are convoluted. For a large n and for times large compared with the inverse of any rate constant, the approximation

$$(k_i/(s + k_i)) = \exp(-s/k_i + s^2/(2k_i)^2) \quad (16)$$

gives

$$A(i,s) = \exp(-st_i + \sigma_i^2 s^2/2) \quad (17)$$

The (two-sided) Laplace inverse of this is a normal distribution centered at t_i and with variance σ_i^2 , and approximate solutions to the n -state model can be built up from these normal distributions. Figure 2.10 illustrates the use of this approximation in modeling a mitotic-yield experiment.

One can go a step further and neglect the variance in Eq. (17), i.e.,

$$A(i,s) = \exp(-st_i) \quad (18)$$

The inverse of this is a Dirac-delta function delayed to the time t_i . The resulting approximation is crude; a synchronized population simply advances in steps from one state to the next without desynchronization. But it is easy to calculate.

FIGURE 2.10. The Normalized Mitotic Yield Rate for a 24-State, Cyclic Model in the Normal Approximation. $q = 2$.

Figure 2.11 shows calculations in this approximation of the mitotic yield of a system in which one of the rate constants was decreased just before cell collection started. Equation (18) suggests another approximation: replace the integer-valued variable i with a continuous variable chosen so $t_i = x$;

$$A(x,s) = e^{-sx} \quad (19)$$

This gives the popular "water-in-a-pipe" model. The variable x plays the role of the "biological time."⁹ This approximation also gives no desynchronization, but Eq. (9) gives the correct stationary distribution, $q w e^{-wx}/(q - 1)$.

Smith and Martin¹⁰ observed that the desynchronization observed in cellular systems may be the result of just one of the rate constants being much smaller than all the others. The theory they developed is a special case of the n -state model in which all but the long-lived state are represented in the "water-in-a-pipe" approximation. When the small- k in a state other than the first one,

$$A(i,s) = (k_i/(s + k_i)) e^{-sx} \quad (20)$$

The additional desynchronization contributed by the other states can be estimated by including the variances as in Eq. (17). The effects of having the small- k in a state other than the first or of having more than

FIGURE 2.11. The Mitotic Yield, Normalized to the Mitotic Yield of the Controls, for a 24-State System in Which the Rate Constant of the 21st State was Decreased just Prior to the Start of Collection. "Water-in-a-pipe" approximation.

one small- k state can also be derived from the present model.

The present purpose for the n -state, cyclic model was to correlate other cell-cycle modeling methods. Certainly, however, it would have been a poor choice if it itself were not a reasonable model for cellular phenomena. Real cellular systems are more complex than the n -state, cyclic model, but often a real network of biochemical pathways can be divided into subnetworks that delay and broaden population waves passing through them as described above. In particular, approximate delay times (t_i) and variances (σ_i^2) can be found and used with the normal approximation, Eq. (17).

Dose Rate Models W. C. Roesch

The literature contains several models for the effects of the dose rate of ionizing radiation on cells. The principal ones are listed below. They give superficially similar survival curves for different dose rates (Figure 2.12): the curves lie between two limiting curves, one for very high and one for very low dose rates; the shapes progress from simple exponential curves at low dose rates to curves with shoulders at high dose rates. The similarity disappears when the type of analysis we employed last year¹¹ is used in studying the effect of dose rate on the survival of *Chlamydomonas reinhardtii*. The results of that experiment together with the theoretical analysis permit rejection of several of the models.

FIGURE 2.12. Survival Curves Calculated from Model 3 for a Very Low Dose Rate and for 2, 4, 8, ..., 1024 rad/min

The models studied were:

Model 1 - Roesch¹² and Kellerer and Rossi.¹³ Any pair of energy deposition events may kill (reproductive death) a cell; the probability of death decreases exponentially with the time between the events.

Model 2 - Swann and del Rosario.¹⁴ Following damage by a first event, a second may kill the cell if it has not recovered in the meantime.

Model 3 - Rajewsky and Danzer¹⁵ and Lea.¹⁶ Death is due to certain pairs of events; the probability is constant for a certain interval after the first one, after which it drops abruptly to zero.

Model 4 - Lajtha and Oliver.^{17,18} Damage is produced continually during an irradiation and, at the same time, may disappear innocuously at a constant rate. The decrease in survival produced by an increment in dose depends only on the amount of damage remaining when the increment is received. This general idea must be supplemented by assuming a specific shape for the limiting survival curve at high dose rates. Two such assumptions were made:

- the high-rate limit from Model 1, and
- that from Model 2.

The analysis employed with *C. reinhardtii* was to plot the negative of the quotient of the logarithm of the survival by the square

of the dose ($-\ln(S)/D^2$) versus the irradiation time. This was done because, in the absence of single-event killing, Model 1 predicts the experimental data will lie on a single curve, regardless of dose rate. The single curve is the heavy line in Figure 2.13, which was calculated for the parameters that best fit the data for *C. reinhardi*. Model 4.a gives the same, single curve as Model 1.

Models 2, 3, and 4.b do not give single curves. They give families of curves similar to the family shown in Figure 2.14, calculated for Model 3 and for parameters that make it coincide with Model 1's single curve in the limit of low dose rates. This choice of parameters is an arbitrary one, but is simple and natural. The choice does not affect the conclusion to be drawn. Figure 2.13 shows the curves for Models 2, 3,

and 4.b for the highest and lowest dose rates used in the experiment.

Model 4.a, which is related to Model 1, gives a curve identical to that for Model 1; but Model 4.b, which is related to Model 2, does not give the same results as Model 2. This peculiarity of the Lajtha-Oliver model was noted earlier.⁸

The data for *C. reinhardi* for different dose rates were judged to lie on a single curve, a curve fitted by Model 1 (see Ref. 11, Figure 2.24). They certainly do not lie on a family of curves such as the one shown in Figure 2.14. Thus, Models 2, 3, and 4.b can be rejected for the recovery phenomena in *C. reinhardi*. Models 1 and 4.a merit further study. Data for mammalian cells⁹ appear to lie on a single $-\ln(S)/D^2$ curve; therefore, the conclusion may apply to some mammalian cells also.

FIGURE 2.13. The Single Curve from Models 1 and 4.a that Best Fits the Data for *C. reinhardi* and the Highest and Lowest Dose-Rate Curves from the Families from Models 2, 3, and 4.b that Would Most Nearly Fit that Data

FIGURE 2.14. The Family of Curves from Model 3 that Would Most Nearly Fit the *C. reinhardi* Data

The successful Models 1 and 4.a differ from Models 2 and 3 in that cells that are damaged, but not killed, may accumulate damage from each energy deposition. Consequently, their probability of being killed at the next deposition increases during the irradiation except as modified by recovery. In Models 2 and 3, once a cell is damaged, it remains unchanged until it recovers or until it receives the further damage that kills it. In other words,

its probability of being killed at the next deposition remains constant during the irradiation except as modified by recovery. This distinction between the damaged states fails in the case of Model 4.a: the Lajtha-Oliver model assumes that damage accumulates. Model 4.a, however, is the offspring of one parent that accumulates damage and one that does not, it might be expected to be rather queer.

• DOSIMETRY OF PARTICULATE SOURCES IN THE LUNG

The purpose of this study is to develop practical methods for calculating microdosimetric distributions for soft tissue and for lung tissue in which plutonium or other alpha-emitting elements are deposited, particularly when deposited as particulates, to aid in correlating and extrapolating 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 Radiological Health Section will develop cell and tissue models in which those methods will be applied. Single-event energy depositions due to alpha particles were studied by Monte Carlo methods. A computer program for combining the single-event depositions due to any distribution of small particulates in soft tissue was prepared.

Calculations for Microdosimetry of Internal Sources

W. C. Roesch

Practical methods for calculating microdosimetric distributions due to internally deposited alpha-particle emitters are being developed in two phases. One is the determination of the energy deposition by single alpha particles; the other, the present subject, is the development of computer programs for combining these single-event depositions for any positions of the emitters. Last year the first version of such a program was prepared. This year that program was completed and generalized to handle any distribution of positions of particulates in soft tissue. A large part of the effort on the first version went into speeding up the calculations. Calculation times were reduced by about another factor of five, and time is no longer an important limitation.

A number of simple examples were studied with the completed program in order to familiarize users of the programs with how they are to be applied, to show what kind of results come from internal

microdosimetry, and to begin applications to simple tissues. The examples used the provisional single-event densities devised last year. Two of the examples will be discussed here to show the problem of data assimilation that arises and one solution to that problem.

Figure 2.15a shows probability densities in specific energy at several distances from a plane surface in soft tissue. Particulates that on the average emitted one alpha particle each were uniformly, randomly distributed in the tissue on one side of the plane in such density to give an absorbed dose of 75 rad. The situation is that occurring at the edge of a tissue that concentrates particulates. Deep on the side containing the particulates the density is the same as if the whole region contained particulates. The area beneath the curves decreases as the plane boundary is approached and passed, reflecting the decreasing chance that a site will be struck by an alpha particle because of the increasing average distance from the emitters.

The decrease in area masks the changes in shape of the curves. To display the shapes, the same densities are replotted in Figure 2.15b after renormalizing them so they all have the same area--in other words, Figure 2.15b gives probability densities conditional on there being some energy deposited. The figure shows that there is little difference in shape for sites on the side containing the particulates. On the other side, the densities shift to higher specific energies, because the site is farther from the emitters on the average. Consequently, when the alpha particles reach the site, they have lower energy and higher stopping power and deposit more energy.

Figure 2.16 shows the densities at three distances from a sphere of $5\text{-}\mu$ radius that contains 100 randomly positioned particulates that on the average emit just one alpha particle each. This situation might occur as the result of breakup of a larger particulate. The dotted lines are the densities that would have been produced at the same distances from the large particulate prior to its breakup. The differences are small. The densities after breakup are shifted slightly to higher specific energies, because, as in Figure 2.15, the average distance between the site and the emitters is larger.

These examples illustrate a problem: the large number of different densities that arise from internally deposited emitters makes assimilation of their significance difficult. No difficulty exists, of course, in making calculations with the large number; the densities must be generated with a large computer anyway and that computer can easily use them in any desired way. But an investigator viewing the densities, trying to decide what they imply or what use to make of them, may be puzzled by the mass of detail.

One way of reducing the detail to more manageable proportions is to calculate the probability density, $g(z)$, for finding the specific energy z in some one site in a group of sites as opposed to finding it in a particular site, the type of density given above. If $c\,dV$ is the probability of finding a site in the volume element dV , then

$$g(z) = \int c\,f(z)\,dV \quad (1)$$

where $f(z)$ is the probability density for any single site in the volume element.

The probability density, $f(z)$, for a single site may be pictured as the frequency distribution resulting from repeated measurements in that particular site.

FIGURE 2.15. (a) Probability Densities in Specific Energy for a Uniform, Random Distribution of Particulates (each of which emits one Alpha Particle, on the Average) on one Side of a Plane Surface, for an Absorbed Dose of 75 rad Deep on the Side Containing the Particulates. X is the distance from the plane and is negative on the side containing the particulates. (b) Densities for the same circumstances, conditional on there being energy deposited.

FIGURE 2.16. Probability Densities in Specific Energy for a Uniform, Random Distribution of Particulates (each of which emits one Alpha Particle, on the Average) in a Spherical Region $5 \mu\text{m}$ in Radius. On the average, a total of 100 alpha particles was emitted in the spherical region. X is the distance from the center of the sphere. The dotted curves are for a single particulate from which the same number of alpha particles was emitted; X is the distance from the particulate.

Similarly, the $g(z)$ -density for a group of sites may be pictured as the frequency distribution resulting from repetitions of a two-step process: first selecting at random a site from the group; second measuring a value of z in that site.

Use of the group density reduces the amount of detail that must be observed, but care must be taken because it may be different for each group of cells for which the integration in Eq. (1) is performed. For example, Figure 2.17a shows the group densities for three groups near the half space for which individual densities are shown in Figure 2.15. One group consists of the sites within the region containing the alpha emitters and lying between the plane boundary and a depth equal to the range of the alpha particles. Another consists of the sites on the other side of the boundary, to a distance equal to the range. The third is the combination of the first two. The different magnitudes of the densities reflect principally, in this case, the different chances of alpha particles striking a site. Inside the emitting region, the chance is high (although less

than 1.0); outside it is relatively low. The combined group contains the sites of both low and high probability of being struck and gives an intermediate density.

Of course, differences between groups are just what an investigator will be looking for to explain differences in biological effects of radiation. So the care is required in defining the groups in the most meaningful way.

The differences in $g(z)$ for different groups can be quite large. Figure 2.18a shows the densities for two groups of sites near the spherical collection of particulates of Figure 2.16. One group consists of the sites inside the sphere; the other, those outside the sphere but within range of the alpha particles. The group density for the sites inside the sphere is centered around quite large specific energies, because sites within the sphere are not only apt to be hit by alpha particles, they are apt to be hit many times. Outside the sphere, the chance of being struck drops rapidly and many sites within the range of the alpha particles are not struck at all (the area under the curve is less than 1.0).

FIGURE 2.17. (a) Probability Densities in Specific Energy for Groups of Sites Some of Whose Individual Densities are Shown in Figure 2.15 (half space). The group marked "inside" are those sites within range of the boundary of the half space on the emitter side; "outside," within range of the boundary on the non-emitter side; the third group is the combination of the first two. (b) Densities for the same circumstances, conditional on there being energy deposited.

FIGURE 2.18. (a) Probability Densities in Specific Energy for Two Groups of Sites, Some of Whose Individual Densities are Shown in Figure 2.16 ($5\text{-}\mu\text{m}$ sphere in which 100 alpha particles were emitted). One group consists of the sites inside the sphere; the other, those outside but within one alpha-particle range of the sphere. (b) Densities for the same circumstances, conditional on energy being deposited.

Densities conditional on there being energy deposited are useful with the group density also in showing changes in curve shape as opposed to changes in the area beneath. Figures 2.17b and 2.18b show the conditional group densities in the two examples just discussed. Differences in conditional group densities tend to be smaller than those between their constituent individual densities because they are averaged out in the integration process defined in Eq. (1).

Single-Event Probability Densities for Alpha Particles

W. E. Wilson

Single-event probability densities are of interest in the microdosimetry of internal emitters (see Ref. 20 and this report). When the size of the absorbing site is large compared to the range of the most energetic

secondaries, radius $\gg 1 \mu\text{m}$, the charged particle path-length distributions dominate the single-event probability densities.²¹ However, when the radius of the site is of order $1 \mu\text{m}$, second-order effects become important. For example, alpha tracks which pass near but outside the site sometimes produce energetic delta rays which can contribute to the energy imparted. We are calculating second order effects to get an improved estimate for single-event probability densities for alpha particles.

We have used Monte Carlo techniques to obtain probability densities for energetic alpha tracks which pass totally outside spherical sites of various sizes. Figures 2.19 and 2.20 show histograms of the contributions for all such events for 3 and 6 MeV alphas passing outside sites of radius 0.5 and $2.5 \mu\text{m}$, respectively. The

FIGURE 2.19. Single Event Probability Densities for 3 and 6 MeV Alpha Particles Incident upon $0.5 \mu\text{m}$ Site Radius. The histogram is from Monte Carlo calculations, the solid lines are model representations of the distributions.

FIGURE 2.20. Single Event Probability Entries for Near-Miss 6 and 3 MeV Alpha Particles for a Site Radius of $2.5 \mu\text{m}$. The histogram is from Monte Carlo calculations, the solid lines are model representations of the distribution.

spectral shape of the distribution is approximately exponential in energy imparted with a characteristic (slope on semi-log plot) that is energy independent; however, the amplitude does depend on alpha energy.

From histograms like those in Figures 2.19 and 2.20 for alpha particle energies ranging from 2 to 6 MeV and for site radii from $0.5 \mu\text{m}$ to $2.5 \mu\text{m}$, we have concluded that a suitable representation of the "near miss" distributions can be obtained from $A \exp(-Be)$, where e is energy imparted and A is a linear function of only alpha energy and B depends linearly of site radius only. The solid lines indicate this model of the distributions for respective alpha particle energies and site radii.

Experimental Microdosimetry for Alpha Particles

L. A. Bräby and W. C. Roesch

In order to test the results of Monte Carlo calculations of single event probability densities and to point out aspects of the theory which need to be strengthened, experimental measurements must be made. One such experiment, designed to complement theoretical work on alpha particle dosimetry, employs radon gas mixed with the counting gas in a wall-less proportional counter.²² In this situation, the radon itself provides a uniformly and randomly dispersed source, but the radon daughter nuclides attach to dust particles and are collected on the surface of the detector and its vacuum

chamber. Thus, there are three monoenergetic alpha sources to be considered: ^{222}Rn at 5.49 MeV, ^{218}Po at 6.002 MeV, and ^{214}Po at 7.687 MeV. By fractionating the counting time and allowing the collected Rn daughters to decay away between counting intervals, it was demonstrated that the ^{222}Rn alpha contributed an insignificant fraction of the measured events. Clearly ^{218}Po and ^{214}Po are being collected from the large volume surrounding the detector. Since the detector is operated with the anode grounded, the detector walls are at approximately minus 900 volts relative to the vacuum chamber walls. The fractions of the two isotopes collected on the detector depend on the electrostatic charge of the particles they are attached to, and this may be different for ^{214}Po which comes from a β decay and ^{218}Po from an α decay.

Expected pulse-height spectra were calculated in order to compare with the experimental results. The alpha emitters were assumed distributed on the surface of a cylinder. The paths of the alpha particles were assumed to be straight lines. The difference in alpha-particle energy for the residual ranges on entering and leaving the counter was assumed deposited in the counter. Straggling effects were simulated by spreading this deposition with a normal distribution.²³ The deposition by delta rays from alpha particles that just missed the counter was not calculated. The calculated spectrum was normalized to fit the data; no normalization was applied to the values of the energies deposited (the abscissa in Figure 2.21).

There is good agreement between experiment and calculation, Figure 2.21, over most of the event-size range. The experimental points are higher than the calculated spectrum at small energies because of depositions by alpha particles that just miss the

FIGURE 2.21. Pulse-Height Spectrum Produced by Radon Daughter Products in a Wall-Less Proportional Counter. Experimental, $\circ$, calculated—.

counter and by ^{214}Pb and ^{214}Bi beta particles. The small excess at the very highest energies is believed due to bulging equipotential surfaces that make the wall-less counter noncylindrical. The presence of the beta particles and the uncertainty in the ratio of the two emitters on the detector walls prevents a detailed investigation of the consistency with experiment.

• RADIATION PHYSICS

The Radiation Physics Program is directed toward providing information on the initial interactions by which ionizing radiation transfers energy to biologically significant matter and the subsequent transport and degradation of that energy. Measurement of differential ionization cross sections provide data to meet two primary needs: 1) to test theoretical descriptions of the ionization process thus enabling a more basic understanding of the energy loss process, and 2) to present the data base required for the development of track structure models used in the study of energy transfer and radiation damage. Theoretical studies of the energy transfer processes in gas and liquid systems are directed toward connecting our knowledge of the basic interaction cross sections with measurements of fluorescence and fluorescence lifetimes in liquids. These investigations of the liquid system include such studies as the quenching of excited states by formation of transient chemical species and the correlation of the LET of the excitation source with the observed fluorescence. This closely correlated program of theoretical studies in energy transfer, measurements of time resolve fluorescence of binary liquid systems, and measurements of initial interaction probabilities utilizing gas targets is expected to provide insight into the mechanisms of radiation damage to biological systems.

• BASIC COLLISION CROSS SECTIONS

Energy Dependence and Inner Shell Effects in Differential Ionization Cross Sections for Fast Protons

L. H. Toburen and S. T. Manson*

The analysis of measured differential ionization cross sections in terms of their ratio to Rutherford cross sections has been discussed in detail by Kim²⁴ for electron impact. By plotting the ratio of the measured cross sections to Rutherford values versus energy loss, one can (according to theory) determine the high energy asymptotic value of the resulting curve from Rutherford theory and the low energy shape of the curve from optical data. The success of this analysis for fast electron impact (500 eV

incident electrons) led to reliable tests of experimental accuracy and to methods of extrapolation of cross sections to regions where data are unavailable.²⁴ Our use of this means of analyzing data for 1 MeV proton impact (equivalent velocity approximately equal to 500 eV electrons) was less successful.²⁵ The disparities which were observed led us to question whether the data were less reliable than expected or whether the proton velocity was too low for the "high energy" approximations of the theories to be valid. To explore the questions more fully, we have extended this work to proton energies of 0.3 and 1.5 MeV. The measurements were made using both electrostatic and time-of-flight energy analysis to insure optimum experimental accuracy throughout the ejected electron energy spectra. The uncertainty in the measured cross sections is expected to be less than $\pm 20\%$ in absolute value and $\pm 10\%$ in relative value.

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An example of the method of analysis suggested by Kim is shown in Figure 2.22 for 1.5 MeV proton ionization of helium. As defined by Kim,²⁴ $Y(E,T)$ is given by

$$Y(E,T) = \frac{TE^2}{4\pi a_0^2} \sigma(\epsilon) \quad (1)$$

where ϵ is the ejected electron energy, E is the energy loss ($E = \epsilon + I$, I being the first ionization potential of the target atom), and T is given by $1/2m_e v_p^2$. Since $Y(E,T)$ is the ratio of measured cross section to Rutherford cross section per electron, the asymptotic value of 2 is to be expected for ionization of helium. The asymptotic value of $Y(E,T)$ shown in Figure 2.22 is in quite good agreement with the expected value. In addition, the shape of the low energy portion of the curve for ionization by sufficiently fast charged particles is expected to be similar to that derived from the optical oscillator strength. This is based on the expression

$$Y(E,T) = E \frac{df}{dE} \ln \left(\frac{4T}{R} C(E) \right) + B(T,E) \quad (2)$$

which is derived from the Born approximation.²⁶ In Eq. (2), $B(T,E)$ is the hard collision contribution, large E , and $C(E)$ is

expected to be a slowly varying function of E . In Figure 2.22, the low energy portion of the curve is indeed in close agreement with the shape derived from the dipole oscillator strength distribution. Ionization of helium by 1.5 MeV protons agrees well with the results expected from theory.

The results of measurements for proton ionization of neon, however, indicate the difficulties which occur for interpretation of data for target atoms which include inner shells. Since neon has a total of 10 electrons, one would expect, according to Rutherford theory, the asymptotic value of $Y(E,T)$ to be 10. As is evident in Figure 2.23, this high energy limit is apparently not yet reached for 1.5 MeV proton impact. This disparity results, in part, to evaluation of Eq. (1) using a single ionization potential, that of the outer shell electrons for all ejected electrons. Although obviously incorrect when electrons are ejected from the K-shell, this method of evaluation is necessary since experimentally there is no way of knowing from which shell the electron originated. If the energy loss were large compared to the K-shell binding energy, this approximation would not effect the results. However, since the maximum ejected electron energies for these proton energies are not sufficiently high for the K-shell binding energy

FIGURE 2.22. The Ratio of Measured Differential Ionization Cross Section to the Rutherford Cross Section Per Electron for Ionization of Helium by 1.5 MeV protons. The normalized oscillator strengths are those of Berkowitz as presented by Kim in Ref. 26.

FIGURE 2.23. The Ratio of Measured Differential Ionization Cross Section to the Rutherford Cross Section per Electron for Ionization of Neon by Protons

to be negligible, the approximation of using the outer shell binding energy for all electrons will, in effect, lead to an underestimation of $Y(E, T)$ compared to the Rutherford estimate. The neon data in Figure 2.23, for example, approaches a value of about 9 instead of the expected value of 10. For lower energy protons, consider the 0.3 MeV data in Figure 2.23: the plateau region is never reached and the Rutherford estimate is of little use in checking the consistency of experimental data.

The shape of the low energy portion of the spectra also shows a dependence on the proton energy. Even for the energy scale used in Figure 2.23, it is evident that the low energy peak in the distribution shifts toward higher electron energies as the proton energy decreases. This shift in the peak energy is in contrast to the constant value expected based on this peak being optical in character, i.e., being describable in terms of the dipole contribution to the Born approximation. The position of the low energy peak for proton ionization of neon is shown in Figure 2.24 for proton energies from 50 keV to 1.5 MeV. The low-energy proton data are from the work of Crooks and Rudd.²⁷ Also shown in Figure 2.24 are the expected results based on the optical nature of the peak, the Hartree-Slater Born calculation of S. T. Manson (Georgia State University) and the position of the peak associated with

electrons ejected by the continuum charge transfer process. It is particularly interesting to note that the low-energy proton data ($E_p \lesssim 300$ keV) exhibit a low energy peak which coincides in energy with the value expected from continuum charge transfer. This may be expected since the maximum effect from continuum charge transfer occurs for low energy protons and provides a large contribution to the spectrum.²⁸ For example, the low energy peak due to charge transfer occurs at precisely the value predicted for the optical maximum for 100 keV proton ionization and this complicates the analysis. One must be cautious not to be confused by the similar shape of the charge transfer contribution to the spectrum and that expected due to the optical nature of the peak for these low-energy protons. From the data in Figure 2.24, it is apparent that the low-energy portion of the ejected electron energy spectra will not be truly optical in shape and character until proton energies of 4 or 5 MeV are reached. This is much higher in energy than expected based on the agreement obtained for electron impact at 500 eV (equivalent velocity to a 1 MeV proton) and points to the need to carefully consider the interaction process involved before considering protons and electrons as equivalent at equal velocities as dictated by simple theoretical models.

FIGURE 2.24. The Position of the Low Energy Peak in the Energy Loss Spectra is Shown as a Function of the Incident Proton Energy. The dashed line is from a Hartree-Slater Born calculation by S. T. Manson of Georgia State University. The proton data for energies below 300 keV are from the work of Crooks and Rudd.²⁷

Energy and Angular Distributions of Electrons Ejected from Water Vapor by 0.3-1.5 MeV Protons

L. H. Toburen and W. E. Wilson

The primary energy loss mechanism in the stopping of fast charged particles is the ionization of the constituent molecules of the media traversed.²⁹ In order to understand the processes of energy deposition by charged particles and their relation to subsequent radiation damage in biological systems, a detailed knowledge of the ionization process is required; these details serve as the data base for track structure models.^{30,31} The importance of the water molecule in the investigation of radiation effects in chemical and biological systems has prompted the study of proton ionization of water vapor.

Cross sections, differential in electron energy and emission angle, have been measured for proton ionization of water vapor (Figure 2.25), oxygen, and hydrogen under identical experimental conditions. A series of consistency tests applied to the cross sections indicate that the precision of the measurement is well within the estimated $\pm 20\%$ uncertainty in the

absolute values. The tests also reveal the importance of the continuum charge transfer process in ionization by protons as contrasted to electron impact ionization. Additivity is found to provide excellent water vapor cross sections for 1.5 MeV proton impact and electron energies greater than 50 eV with differences increasing as the proton energy decreases. Additivity reproduces well the double differential cross sections at emission angles near the binary encounter maximum, whereas scaling oxygen and water vapor according to the number of weakly bound electrons in the respective molecules works best at large and small angles with the largest disparity at the binary encounter peak. Both additivity and scaling work well for single differential cross sections for ejected electron energies greater than about 100 eV. Below 100 eV, molecular structure plays an important role in establishing the electron energy spectrum. The details of this investigation have been submitted for publication.

FIGURE 2.25. Product of Ejected Electron Energy and the Emission Cross Section, $\epsilon\sigma(\epsilon, \theta)$, Differential in Electron Energy ϵ and Emission Angle θ , for Ejection of Electrons from Water Vapor by 1.0 MeV Protons

Differential Ionization of Noble Gases and Water Vapor by Helium Ions and Alpha Particles

L. H. Toburen, R. J. Popowich,* and W. E. Wilson

The need for quantitative information regarding the interaction of helium ions and alpha particles has been emphasized by recent studies regarding radiation damage due to radioactive particles in the lung. Track structure models needed to provide energy deposition distributions rely on accurate interaction cross sections which cover a wide range of particle energies and target material as well as various charge states of the penetrating particle. We have undertaken the study of differential ionization of noble gases by helium ions and alpha particles in order to examine the

systematics of the interactions where the guidance afforded by theory is expected to be the most productive. We are particularly interested in determining the possibilities of scaling proton data, where cross sections are now abundantly available, by Z^2 , or other means, to provide the required information for track structure calculations.

Preliminary analysis of data for 1.2 MeV helium ion and alpha particle ionization of helium, neon, and argon has included comparison of the energy distributions of ejected electrons to those from equal velocity proton impacts. The presentation of the data in terms of the parameters $Y(E, T)$, as discussed in the preceding article, provides an illustration of the effects of the nature of the projectile on the electron energy spectrum. In Figure 2.26, a comparison of equal velocity H^+ , He^+ , and He^{++} ionization of helium is presented. In this illustration, $Y(E, T)$

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FIGURE 2.26. The Ratio of Measured Differential Ionization Cross Section to the Rutherford Cross Section per Electron is Presented versus R/E for Ionization of Helium by Equal Velocity Protons, Helium Ions, and Alpha Particles

is plotted versus R/E which serves to emphasize the low energy end of the electron spectra where the major projectile charge dependence is observed. It need be stressed that, since these data are from electrostatic energy analysis with no time-of-flight results yet available, the data for electron energies less than 10 eV are not reliable; above 10 eV uncertainties are expected to be less than $\pm 20\%$ absolute and $\pm 10\%$ relative. The representative error bars shown in Figure 2.26 are estimated uncertainties in the relative values obtained in this measurement.

The most outstanding feature illustrated in Figure 2.26 is the wide difference in the spectra for He^+ and He^{++} impact. One might expect the enhancement of the H^+ spectra near 150 eV ejected electron energy as being due to electrons which are stripped from the incoming projectile. The wide differences at lower energies is not, however, as obvious. The dependence on energy loss of the difference between the He^+ and He^{++} induced spectra may best be described in terms of a screening parameter which

depends on the energy loss. In this description the small energy losses, associated with large impact parameters, occur at distances such that the incident He nucleus is largely screened by the bound electron and looks much like a proton in its ability to eject an electron from the target atom. For large energy losses, the associated impact parameter is small and the ejected electron is initially near the nucleus of the incoming ion such that the projectile is screened very little by its bound electron. This is supported by the nearly exact agreement between spectra for He^+ and He^{++} for ejected electron energies near and above about 500 eV. The important conclusion from this comparison is that one cannot apply a simple scaling procedure to proton data to obtain the energy spectra of electrons from He^+ . This is true even if account is taken of the stripped electron by adding its contribution to the spectrum at the proper electron energy. We are presently extending this analysis to neon and argon data and plan to investigate the projectile velocity dependence in the near future.

We have also initiated a study of He^+ and He^{++} ionization of water vapor. Since living tissue is about 80% water, radiation damage from α particles is expected to occur either directly or indirectly through interaction with water molecules. Current methods of dosimetry often use stopping power to determine the amount of energy deposited and thus the dose received in a material. Although there are considerable stopping power data available for protons, not much has been done for heavy ions. A theoretical extrapolation is generally made for heavy ions using a z^2/v^2 dependence, where z is the charge and v is the velocity of the incoming particle. This extrapolation, although useful at higher velocities, is known to fail at low velocities where charge transfer becomes important. Charge transfer occurs near the end of the ions path when having lost much of its energy, it is moving slowly and the probability of picking up an electron increases.

Preliminary data for 1.2 MeV helium ion and alpha particle ionization of water vapor is shown in Figure 2.27. These are illus-

trated similarly to the helium data in Figure 2.26, and the same general description applies. It is clear that no single scaling factor can be found to extrapolate proton data to either He^+ or He^{++} data. The scaling factor between these seems to be energy dependent (and not a simple z^2/v^2 relation) and might be explained in terms of the screening effect of the bound electron associated with the He^+ ion; this was discussed above with regard to the helium data.

Although it is evident from Figure 2.27 that proton data do not scale to He^{++} by a simple z^2 rule for energy loss less than about 100 eV, the mean energy of the ejected electrons is quite similar for equal velocity protons and alpha particles. The mean energy deposited to electrons by 0.3 MeV protons and equal velocity alpha particles is 45.5 eV and 48.9 eV, respectively, whereas for He^+ this value increases to 74.0 eV. These values emphasize the difficulty in estimating track structure parameters for helium ions based on scaling proton data. These measurements are now being extended to other ion energies available from our 2 MV accelerator.

FIGURE 2.27. The Ratio of Measured Differential Ionization Cross Section to the Rutherford Cross Section Per Electron is Presented Versus R/E for Ionization of Water Vapor by Equal Velocity Protons, Helium Ions, and Alpha Particles

Potential Barrier Effects in the Ionization of Symmetric Molecules

L. H. Toburen and W. E. Wilson

The high degree of symmetry in molecules such as SF_6 and TeF_6 has been discussed by Dehmer³² as leading to effective potential barriers in the neighborhood of the electronegative atoms in the molecules. Such a "two-well" potential leads to possible bound states when the electron is between the electronegative outer atoms and the electropositive central atom and further discrete states when the electron is at large distances from the molecular ion. The two-valley potential thus leads to "inner" and "outer" well states with small probabilities of transition between these states. This model has been used successfully by Delmer to interpret strong absorption lines observed in photoionization spectra and to explain the absence of Rydberg structure in symmetric molecules such as SF_6 , BF_3 , H_2S , etc.

The effect of potential barriers in the electron spectra for ionization of symmetric molecules has not been previously investigated. The present measurements were undertaken to look for effects of the potential barrier in TeF_6 and SF_6 . In Figure 2.28 are shown the low energy spectra of electrons ejected at 90° in ionization of SF_6 , TeF_6 , and Xe by 1.8 MeV protons. The xenon spectrum is used to provide an accurate calibration of the energy scale based on structure due to autoionization at very low electron energies. This structure is shown in greater detail in Figure 2.29. The peaks labeled A, C, E, and G agree in energy to within 75 meV of the energies for excitation of the 6d, 7d, 8d, and 9d autoionizing Rydberg levels, respectively, leading to the $^2P_{1/2}$ ionization limit as reported by Comes, et al.³³ The positions labeled B, D, and F correspond to excitation of the 8s, 9s, and 10s levels of the corresponding Rydberg series. This comparison provides confidence in our ability to determine electron energies to 0.1 eV in these measurements.

The well resolved peak at 6 eV in SF_6 and the shoulder on the TeF_6 spectrum at 5 eV coupled with the lack of Rydberg structure support the description of these molecules in terms of effective potential barriers. Based on the description of Dehmer, the symmetry allowed dipole transition from the $5a_{1g}$ state of SF_6 to the $6t_{1u}$ state would occur with an energy transfer of 23.8 eV. This transition appears as

a strong feature in the energy loss spectrum for electron impact observed by Simpson, et al.³⁴ Since this excitation is above the ionization potential of SF_6 (15.8 V), one would expect the excited molecule to de-excite through autoionization with the release of an 8 eV electron. The measured energy of the peak in the SF_6 spectrum shown in Figure 2.28 is 6 ± 0.1 eV. We attribute this lower energy, as well as the width of the peak, to dissociation of the SF_6 molecule accompanying autoionization. This interpretation is further supported by the mass spectroscopic studies of Dibeler and Mohler³⁵ who observe the appearance of SF_2^+ with electron impact on SF_6 at 26.8 eV.

Ionization by Protons: 5 to 50 keV

T. L. Criswell* and L. H. Toburen

Initial measurements of double differential ionization cross sections for protons on argon have been completed and are to be submitted for publication in the open literature. These measurements have proven the accuracy of the new low-energy ionization facility and contributed to our understanding of low-energy collision mechanisms. It was found (see Figure 2.30) that a large fraction of the ejected electron yield for 10 keV protons comes from autoionization of argon. Analysis is presently underway to determine which autoionizing states are being populated and what the excitation functions of these states are. Measurements have also been completed for ionization of argon by H_2^+ ions. These data indicate that different autoionization states are populated by H_2^+ compared to proton bombardment. The ratio of cross sections for equal velocity H^+ and H_2^+ ionization is also being studied to determine the role of the electron, which is bound to the hydrogen molecule in the collision process. Measurements have recently been made for proton ionization of nitrogen gas; proton energies from 5 to 50 keV. Preliminary analysis indicates that the general trends in the direct electron-ejection cross sections parallel those observed for argon, while the contribution due to autoionization is small. Detailed analysis of these data is now underway.

* Temporary assignment.

FIGURE 2.28. Electron Energy Spectra Observed at 90° for Ionization of SF₆, TeF₆, and Xe by 1.8 MeV Protons

FIGURE 2.29. Low Energy Portion of the Electron Energy Spectrum for Ionization of Xenon by 1.8 MeV Protons. Peaks labeled A, C, E, and G are attributed to excitation of the 6d, 7d, 8d, and 9d autoionizing levels and peaks B, D, and F to the 8s, 9s, and 10s levels, respectively, leading to the $2P_{1/2}$ ionization limit.

Molecular Effects in Inner Shell Ionization

L. H. Toburen, D. J. Lynch,*

R. P. Chaturvedi,** and W. E. Wilson

The determination of inner shell ionization cross sections from measured Auger electron yields is particularly important when the relevant fluorescence yield is small. For elements with atomic numbers less than ten, the K-shell ionization cross section can be obtained with an accuracy limited primarily by the ability to determine the Auger electron yield; for these elements, the K-shell fluorescence yield is less than 1%. The K-shell ionization cross sections measured for these low-Z elements normally rely on data from either solid or molecular targets. Although the K-shell binding energy is much greater than the valence binding energy, there still is evidence that K-shell vacancy production may depend on the molecular environment.^{36,37}

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It becomes difficult, therefore, to interpret differences observed between results of measurements which have used different molecular forms of the target atom or between results of measurements and calculations where the calculations are for free atoms.

Recent measurements regarding the K-shell ionization cross sections for fluorine by fast protons again pose the question regarding the extent to which the molecular environment may influence the results. Results presented by McKnight and Rains³⁸ are smaller (~20%) and those of Kobayashi, et al.³⁹ are larger (20-50%) than our published measurements;⁴⁰ McKnight and Rains used SF₆, Sobayashi, et al. used CCl₂F₂, and we had used BF₃ as the fluorine target. In order to investigate the effects of molecular environment of the fluorine K-shell ionization cross sections, we have recently measured fluorine Auger yields for the molecular targets BF₃, CF₄, C₂F₆, SF₆, and TeF₆. Gas pressures were measured by a capacitance monometer and all experimental parameters remained fixed except for changing gas. In this way, relative cross sections could be measured with uncertainties less than ±5%. The results of this measurement, which were carried out for proton

FIGURE 2.30. Electron Energy Distributions for Low-Energy Proton Impact Ionization of Argon. The Behlen data is unpublished results of M. E. Rudd, University of Nebraska.

energies of 0.5 and 1.5 MeV, were that cross sections for all molecules except SF_6 fell within the $\pm 5\%$ experimental uncertainties. The SF_6 results fell consistently lower than the rest of the data by approximately 10%. In general, these measurements indicate a lack of influence by the molecular environment on the K-shell ionization cross section. The 10% variation of the SF_6 cross sections from the other molecules studied, although significant, is not adequate to create the differences observed between previous measurements.

Analytical Expression for Cross Section Data W. E. Wilson

Development of a semi-empirical phenomenological model of the cross sections for electron ejection from poly-atomic molecules has been continued in order to provide an analytical representation of the initial proton ionization process in track structure calculations.

We have extended the modeling described in last year's annual report⁴¹ to proton

energies of 0.3, 1.0 and 1.5 MeV. The mathematical formalism for modeling the double differential cross sections (DDCS) is similar to that used for 0.5 MeV proton data. One minor difference has been introduced to take advantage of a more natural unit for the energy loss. We have found that if energy loss $(E + I_p)$ is expressed in units of $4T$ rather than Rydbergs, then parameterizing the coefficients for different proton energies is considerably simplified. The DDCS are scaled according to

$$Y(\theta, E) = \frac{4T^3 [(E + I_p)/4T]^2}{\pi a_0^2 R^2 N_e} \sigma(\theta, E) \quad (3)$$

The $Y(\theta, E)$ defined by Eq. (3) is identical with that used previously.⁴¹

The same empirical non-linear analytical expression previously discussed for 0.5 MeV data, i.e.,

$$Y(\theta, E) = A_1 e^{-Z(\theta)} + A_4 + A_5/K(\theta) \quad (4)$$

where

$$Z(\theta) = [(\cos(\theta) - A_3)/A_2]^2 \quad (5)$$

and

$$K(\theta) = \sqrt{\frac{M_e}{2}} \left[v_p^2 + v_e^2 - 2v_p v_e \cos(\theta) \right]^{1/2} \quad (6)$$

provides a reasonable simulation of the DDCS at the other proton energies as well.

We are now parameterizing the functional dependence of the coefficients on the energy loss and proton energy from the least squares fits to the angular distributions for various energy losses and for the four different proton energies. Figure 2.31 shows the dependence of the coefficient A_2 on energy loss for the proton energies 0.3-1.5 MeV. From these data, one can conclude that A_2 may be represented by $\log A_2 = m \log [(E + I_p)/4T] + b$, where m and b are in general functions of E_p , however, m does not exhibit a strong dependence on E_p .

Likewise, Figure 2.32 shows the functional dependence of A_3 on energy loss for the four energies, 0.3 through 1.5 MeV. The log of the quantity on the ordinate in Figure 2.32 depends linearly on the log of energy loss. The ordinal quantity represents a deviation from classical emission of the electron. If the ejected electron were emitted in a pure

FIGURE 2.31. Coefficient A_2 as a Function of Energy Loss for 0.3-1.5 MeV Protons in H_2O

FIGURE 2.32. Coefficient A_3 as a Function of Energy Loss for 0.3-1.5 MeV Protons on H_2O

classical manner, the ordinal value would be 0, and hence, small ordinal values would represent more nearly binary encounter emission. The dependence of the quantity on proton energy is correct since the quantity is smaller for progressively higher energy protons. The quantity decreases for increasing energy loss as it should for harder collisions.

Coefficients A_2 and A_3 are the easiest coefficients to parameterize. Figures 2.33a and 2.33b show a less favorable situation for which we have not yet found adequate solution. Figure 2.33a presents the coefficient A_1 versus energy loss for the four proton energies for losses $(E + I_p)/4T < 0.4$, and Figure 2.33b shows the same coefficient for energy losses $(E + I_p)/4T > 0.4$. We have, so far, been unable to invent a single parameterization of the coefficient A_1 that is valid over the whole range of energy loss.

FIGURE 2.33a. Coefficient A_1 as a Function of Energy Loss for Small Energy Losses for 0.3-1.5 MeV Proton on H_2O

Coefficients A_4 and A_5 obtained from least squares fitting the data are less well behaved in their dependence on energy loss and proton energy, but the cross sections are not strongly influenced by these terms and hence a more crude representation should be adequate.

Using the parameterization described above for the various coefficients as functions of the energy loss and proton energies, a preliminary analytical expression has been constructed to model DDCS for arbitrary secondary electron energy and for proton energies $(0.3 < E_p < 2 \text{ MeV})$. Figure 2.34 shows a 3D plot of the stopping cross section generated with this preliminary model.

FIGURE 2.33b. Coefficient A_1 as a Function of Energy Loss for Large Energy Losses for 0.3-1.5 MeV Protons on H_2O

FIGURE 2.34. Stopping Cross Section Calculated from Preliminary Model for the DDCS for 1 MeV Proton on H_2O

• RADIOLUMINESCENCE STUDIES

Experimental Radioluminescence Studies
M. L. West and J. H. Miller

Radioluminescence studies continue to emphasize the accumulation and modeling of fluorescence data as a useful technique for examining the effects of chemically active species originating from primary energy deposition in the early stages of radiation interaction in condensed systems. This technique has been used successfully^{4,2} to demonstrate the quenching of benzene fluorescence by transient species produced under proton bombardment. The success of this technique in explaining non-exponential decay has encouraged us to investigate in more detail the general applicability of this model.

The effects of linear energy transfer (LET) on quenching processes in condensed media were obtained from measurements of fluorescence response for incident proton energies of 0.6-1.9 Mev. Dynamic quenching processes resulting from diffusional quenching of chemical species created along particle tracks are investigated from detailed analyses of fluorescence decay curves obtained by single photon counting techniques. Additional quenching processes which may affect the primary yield of excited states or which may occur too rapidly to be detected by our system are studied from total fluorescence intensity measurements.

Fluorescence decay curves and total light intensity measurements were obtained for solutions of benzene (0.04 M) in

cyclohexane at 20°C. Additional data are being taken to ensure a reliable estimate of nonstatistical errors associated with experimental or data fitting procedures. Typical fluorescence decay curves are shown in Figure 2.35 for incident proton energies of 0.85 and 1.9 MeV. Changes in fluorescence quenching with proton energy are evident from this data. Incident protons of 0.6 MeV are sufficiently low in energy to investigate the predicted decrease in quenching near the end of a proton track. Experimental difficulties associated with these measurements include precise determination of energy loss in the entrance foil, detection system resolution and beam intensities as well as maintenance of temperature stability of the irradiated sample.

Uncertainties in foil thickness and unknown stopping powers make theoretical calculations of energy loss questionable. The maximum incident proton energy at which the beam is totally stopped inside the entrance foil was experimentally determined to be 0.55 MeV. This compares to a calculated value of 0.58 MeV. At 0.6 MeV incident proton energy, these two values give a factor of three difference in estimated energy deposited in the liquid. Our present technique of measuring foil thickness through fluorescence cutoff may be in error because of particle straggling (~ 15 keV) or because of electron emission from the foil. Techniques using a surface barrier detector to measure transmission is being considered for future experiments.

FIGURE 2.35. Fluorescence Decay of Benzene in Cyclohexane for Excitation by 0.85 MeV and 1.9 MeV Protons

At present, interpretations at low incident proton energy must include a large error in transmitted proton energy.

Temperature stability also becomes a problem at these low incident proton energies. At 0.6 MeV less than 100 keV of energy is deposited in the liquid and experimental measurements required 4 hr of data accumulation. A cooling-heating system under thermistor control was designed and built to hold sample temperature to within an acceptable tolerance of $\pm 0.2^\circ\text{C}$.

A time resolution of 1 nsec for our present system does not allow us to investigate fast energy transfer processes between solvent and solute nor does it allow us to search for additional rapid quenching mechanisms that may possibly contribute to a reduced fluorescence intensity. Present limitations are dictated by phototube response. In principle, earlier times can be probed if the resolution is improved or if the shape of the resolution function is accurately known. Unfolding techniques could then be used to deconvolute the phototube response from fast decaying scintillators of known decay shape (ideally, exponential decay). Present phototubes designed for fast timing are plagued by secondary peaks in the single electron response. Their sensitivity to environmental conditions make it extremely difficult to obtain a reliable resolution function. We have experimentally studied these secondary peaks in detail and after several discussions with W. D. Lindley (Phototube Application Engineer for RCA at Lancaster, PA), have purchased an experimental phototube designed to eliminate this problem. Additional features include an improved single electron response (0.5 nsec) and low noise (~ 10 cts/sec).

Successful unfolding of the system response depends on an experimental measurement of fluorescence decay of a fast scintillator of known decay shape. Ethroysin B with a reported lifetime of 110 psec was found to have a slower decay component under proton irradiation. Emission from cyclohexane has been used previously to estimate the system resolution but does not appear to be suitable for a detailed unfolding. There is a slower decaying component that has been shown to be sensitive to oxygen quenching. At present, we have not found a satisfactory solution of known fluorescence decay shape. We are considering the use of a (ρ, γ)

reaction with a Cerenkov radiator. Low light intensities may limit the usefulness of this technique.

Total light intensity measurements require an accurate relative determination of proton beam current and geometrical solid angle. Relative beam current measurements at different energies can be affected by electron scattering and changes in beam density. We are redesigning our system to try eliminating these possible sources of error so that reliable comparisons can be made between total light intensity and decay curve measurements.

Fluorescence Quenching Model J. H. Miller and M. L. West

In Figure 2.35, we compared the fluorescence decay of benzene in cyclohexane at two proton beam energies. The decay is not exponential, but approaches an exponential decay with a lifetime approximately equal to that observed with uv excitation⁴³ as time increases. The deviation from exponential decay increases as the proton energy decreases. The nonexponential character of these fluorescence decays has been attributed to the quenching action of transient radical species.⁴² The magnitude of the quenching rate is proportional to the local concentration of radicals which decreases with time after irradiation due to diffusion and radical recombination. The initial concentration of quenchers should be proportional to the linear energy transfer (LET) of the radiation which increases as the proton energy decreases for energies in the range exhibited in Figure 2.35.

To investigate these ideas quantitatively, we have developed an analytic, one-radical model based upon solution of the coupled diffusion equations:

$$\frac{\partial C_*(r,t)}{\partial t} = D\nabla^2 C_*(\vec{r},t) - kC_*(\vec{r},t) - k_{R*} C_{R*}(\vec{r},t) C_*(\vec{r},t) \quad (1.a)$$

$$\frac{\partial C_R(r,t)}{\partial t} = D\nabla^2 C_R(\vec{r},t) - k_{RR} C_R(\vec{r},t) \quad (1.b)$$

which express the competition between fluorescence with lifetime k^{-1} , quenching with rate constant k_{R*} and radical recombination with rate constant k_{RR} . Cyclohexyl $\cdot C_6H_{11}$ is the most likely candidate for the

quencher due to the predominance of this radical in the radiolysis of cyclohexane. Quencher and fluoroscor are assumed to have the same diffusion coefficient which is estimated from the temperature and viscosity of the solvent.⁴⁴

To find the time and spatial dependence of the concentration of excited states $C_*(r,t)$ and radicals $C_R(r,t)$, we must solve Eq. (1.a) and (1.b) subject to an initial boundary condition. Integrating $C_*(r,t)$ over all space gives the population of excited states $N_*(t)$, which is proportional to the fluorescence intensity. By treating the proton track as a collection of cylindrically symmetric segments which evolve in time without interactions, and solving Eq. (1.a) and (1.b) for each segment by the prescribed diffusion approximation,⁴⁵ we obtained the result

$$\frac{N_*(t)}{N_*(0)} = \exp(-kt) \left[1 + \alpha \log \left(1 + \frac{2Dt}{r_0^2} \right) \right]^{-k_{R*}/k_{RR}} \quad (2)$$

$$\text{with } \alpha = g_R \frac{k_{RR}}{8\pi D} \frac{\bar{S}}{100 \text{ eV}} \quad (3)$$

where g_R is the radical yield per 100 eV of energy absorbed, $\bar{S}$ is average stopping power of protons in the liquid, and r_0 is the width of the initial distribution of the chemical species perpendicular to the track axis.

We have used the method of non-linear least-squares to find values of g_R , r_0 , and k_{R*} which give a good fit between Eq. (2) and the experimental decay curves. To determine the extent to which the goodness of fit criterion can be used to estimate these unknown parameters of the model, the chi-square surface was constructed for a region of the parameter space which contained physically reasonable values. Given values of r_0 and g_R , the optimum choice of ratio k_{R*}/k_{RR} may be determined by linear least-squares if k is assumed to have the value determined from uv measurements. In Figure 2.36, we illustrate this optimum choice of k_{R*}/k_{RR} and the resulting value of chi-square by contours in the plane of g_R and $r_0^2/2D$. Points inside the contour $\chi^2 = 280$ represent choices the parameters for which the mean chi-square per data point is less than unity. Since this contour is open, we have concluded that the goodness of fit criterion is insufficient to determine all three of the unknowns, g_R , r_0 , and k_{R*} .

FIGURE 2.36. Contour Plot of Chi-Square Hypersurface

An independent determination of one of these parameters is required. Due to the unpaired electron, we expect $\cdot\text{C}_6\text{H}_{11}$ to be an effective quencher of benzene fluorescence. Hence, we use the diffusion limit⁴⁶ to estimate a value of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for k_{R^*} . Using experimental values^{47,48} of k_{RR} , this implies that k_{R^*}/k_{RR} should have a value in the range of 2-5. From Figure 2.36, this choice of k_{R^*}/k_{RR} implies that g_R is approximately 3 and $r_0^2/2D$ is approximately 5 nsec.

The change in LET [denoted by $\bar{S}$ in Eq. (2)] is expected to be the principal source of the energy dependence of the fluorescence decays shown in Figure 2.35. To test this hypothesis, we fitted the time dependence of the emission at several beam energies with the functional form given in Eq. (2) and compared the change in the coefficient of the logarithmic term with calculated variations in $\bar{S}$. The result is shown in Figure 2.37. The ordinate in Figure 2.37 is the proton energy when it enters the liquid, which is determined from the beam energy after a correction for energy loss in the entrance foil. Uncertainty in the foil thickness is 5%. The uncertainty in the stopping cross sections for constituents of the foil also contribute to the error in calculating the energy loss in the foil. The horizontal error bars on the data points in Figure 2.37 indicate the error in the ordinate

which results from a 10% uncertainty in foil stopping power. The solid curve in Figure 2.37 is the calculated value of the

dimensionless ratio $g_R \frac{k_{RR}}{8\pi D} \frac{\bar{S}}{100 \text{ eV}}$, with

$g_R k_{RR}/8\pi D$ equal to $4 \text{ \AA}$. This value was selected to give the best overlap between the solid curve and the data points. If $k_{RR} = 2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ (see Ref. 47), and $D = 1.3 \times 10^{-5} \text{ cm}^2/\text{sec}$ (see Ref. 43), then g_R is approximately 3. The stopping cross section of cyclohexane for protons was estimated using the Brice formulation with parameters derived from stopping power measurements in CH_4 gas.⁴⁹ Note that the calculated LET decreases when the energy deposited in the liquid is less than 0.15 MeV.

The data points in Figure 2.37 are coefficients of the logarithmic term in Eq. (2) which gave the best fit to the data. The ratio k_{R^*}/k_{RR} was held fixed at a value of 2.5. The vertical error bars indicate the range of variation in the fitting parameter for several sets of data at the same temperature and proton beam energy. Above 0.3 MeV, the energy variation of the fitting parameter is in good agreement with the calculated change in LET. Data at the lowest two energies investigated suggest a decrease in quenching but the effect is not as pronounced as the calculated decrease in

FIGURE 2.37. Calculated and Observed Change in Fluorescence Quenching Parameter α in Equation (2) with Energy Deposited in the Liquid

LET. This may be due in part to the neglect of straggling in these calculations.

Values of r_0 , the initial track radius, which gave the best fit between Eq. (2) and fluorescence decays at the proton energies investigated, are presented in Table 2.1. The fact that r_0 is approximately independent of energy is consistent with the conclusions of Mozumder, et al.⁵⁰ concerning the track structure of heavy ions in this energy range. The magnitude of r_0 determined by fitting the fluorescence decay is influenced by the value assumed for k_{R^*}/k_{RR} , as shown in Figure 2.36, and by the value of the diffusion coefficient. Nevertheless, we feel that the results of this study are in reasonable agreement with the value of 15 Å predicted by Mozumder, et al.⁵⁰ for ions with energy less than 2 MeV/amu in water.

We have investigated the change in fluorescence decay over the full range of proton energies available from the 2 MV accelerator. The results of this study give strong support to the validity of the quenching model. This model may also be used to predict the effects of dynamic quenching on the steady state emission. Comparison of the observed energy dependence of steady state emission with that predicted on the basis of dynamic quenching

TABLE 2.1. Energy Variation of the Initial Track Radius

E_p (MeV) (a)	$E_p - \Delta$ (MeV) (b)	r_0 (Å) (c)
1.90	1.68	23.5
1.70	1.46	22.6
1.25	0.97	22.6
0.85	0.47	23.8
0.75	0.13	24.0
0.60	0.03	23.6

- a. Beam energy
b. Beam energy less energy loss in entrance foil (approximate).
c. Model parameter [see Eq. (15)].

and energy loss in the entrance foil may provide additional constraints on the parameters of the model, or may point to additional quenching mechanisms not included in the model. This work is currently in progress.

Additional experimental tests of the model with more energetic ions available at the University of Washington Nuclear Physics Laboratory are being planned. With more energetic protons, we expect an increase in the initial track radius and a

deviation from results based on the assumption of a cylindrically symmetric track structure.⁵¹ We also hope to compare the fluorescence decay of liquids excited by radiations with the same LET but different particle velocities, as Sauer, et al. has done in absorption studies.⁵² Through studies of this type, we hope to gain more insight into the significance of track structure for energy transfer processes at early times.

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CHARACTERIZATION, MEASUREMENT, AND MONITORING

- **RADIATION INSTRUMENTATION - RADIOLOGICAL CHEMISTRY**
- **ENVIRONMENTAL POLLUTION ANALYSIS - INSTRUMENTS AND METHODS DEVELOPMENT**
- **OIL SHALE AND TAR SAND RESEARCH**
- **DOSIMETRY OF INTERNAL EMITTERS**
- **ANALYTICAL TECHNIQUES FOR ^{99}Tc MEASUREMENT IN ENVIRONMENTAL SAMPLES**
- **TRACE CONSTITUENT ANALYSIS BY LASER EXCITATION**
- **APPLICATIONS OF HOLOGRAPHY**
- **REAL-TIME MEASUREMENT OF Pu IN AIR AT BELOW MPC LEVELS**

• RADIATION INSTRUMENTATION—RADIOLOGICAL CHEMISTRY

Program efforts were concentrated in the following areas: development of low-level radiochemical laboratory techniques, in situ monitoring techniques, and activation analysis technology.

Four different techniques were evaluated for borehole analysis of uranium and thorium ores. These involved the detection of fission product photons after ^{252}Cf activation, the detection of low-energy gamma rays, the direct measurement of the 1001 keV photon from ^{242}mPa , a ^{238}U daughter, and isotopic excitation X-ray fluorescence spectroscopy. X-ray fluorescence spectroscopy and detection of uranium daughter photons allowed 0.01% uranium to be detected. X-ray spectrometry of rare earth elements following activation analysis also allowed better elemental detection sensitivities to be obtained than did the detection of high-energy photons identified with a Ge(Li) detector in typical instrumental neutron activation analysis.

An activation analysis facility is under development utilizing ^{252}Cf in a ^{235}U -fueled subcritical assembly. This assembly will be used to develop cyclic activation analysis techniques for some 65 elements in environmental matrices with sensitivities varying from parts per million to parts per billion.

A study was initiated to identify instrumentation required for the measurement of trans-uranium elements associated with power reactor fuels. Transuranium isotopes, ^{237}Pu , ^{238}Pu , ^{239}Pu , ^{241}Am , ^{243}Am , and ^{244}Cm can be identified through low energy photons or X-rays emitted following alpha emission with planar intrinsic Ge detectors.

High Sensitivity Isotope Analysis with a ^{252}Cf - ^{235}U Fueled Subcritical Multiplier and Low Background Photon Detector System
N. A. Wogman, H. G. Rieck, J. C. Laul and K. W. MacMurdo*

Subcritical multiplication of ^{252}Cf neutrons has proven to be a straightforward and safe method of providing a relatively inexpensive activation facility. It helps solve the problem of economically achieving relatively high neutron fluxes with a limited amount of ^{252}Cf . It also allows the use of these neutrons for a wide variety of neutron

activation and neutron radiography studies in static or portable modes. Use of the multiplier units with high-sensitivity gamma ray spectrometers should greatly expand the application of neutrons in industrial, medical and research applications which cannot presently be met because of the high cost of reactors or the limited supply of the man-made neutron source, ^{252}Cf . A ^{252}Cf activation analysis facility is being completed for routine multi-element analysis of a wide variety of solid and liquid samples (see Figure 3.1). The detection limits for over 65 elements have been calculated for this system with over 40 elements detectable at the 1 ppm level with a precision of $\pm 10\%$.

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FIGURE 1. The Subcritical Multiplier is Housed in a Water Pit for Radiation Shielding and an Operator Can Remotely Position the 100 mg ^{252}Cf Source to Initiate Long-Term Neutron Irradiations

The activation analysis facility will contain 6 sources of ^{252}Cf totalling slightly over 100 mg. These sources will be placed in a 93% ^{235}U -enriched core which is subcritical with a K effective of 0.985 (multiplication factor of 66). The system should produce a thermal flux of 3.5×10^{10} n/cm²/sec. The pneumatic rabbit system will permit automatic irradiation, decay, and counting regimes. Activated isotopes will be analyzed by their photon emissions with state-of-the-art intrinsic Ge detectors, Ge(Li) detectors and NaI(Tl) multidimensional gamma ray spectrometers. High efficiency (25%) low background anticoincidence shielded Ge(Li) detector systems have been constructed to provide the lowest possible background, yet maintain a peak-to-Compton ratio of greater than 1000:1. The multidimensional gamma ray spectrometer systems are composed of two 23-cm-diameter

x 20-cm-thick NaI(Tl) activated crystals surrounded by NaI(Tl) activated anticoincidence shields.

A measurement was made of the neutron flux and energy spectrum arising from a mockup of the subcritical facility using Cu and Cd-covered Cu foils. A flux of 3.5×10^{10} n/cm²/sec was estimated for the central flux trap. This is equivalent to a multiplication factor of 20. The fast neutron multiplication factor was 23.3 at the central flux trap. At the outer edges of the subcritical assembly, the thermal neutron multiplication factor was 109 and fast neutron multiplication factor was 242. The flux variation from center to outside is 3.17. In the central flux trap, the flux varies 1% over a 5 cm distance near the center and 30% over a 20 cm distance at the center.

In addition to the fast rabbit facility (see Figure 3.2) which allows cyclic activation analysis to proceed, there will be two 10-cm-diameter irradiation tubes and four 5-cm-diameter irradiation tubes. On this tube circumference, the thermal neutron flux is about 10^{10} n/cm²/sec with a thermal-to-fast ratio of 110. The thermal-to-fast ratio at the central flux trap is about 33.

Normally, reactor neutron activation analysis is performed at thermal fluxes of about 10^{13} n/cm²/sec using sample sizes of a few milligrams. When a 1000-fold larger sample

is available, neutron activation can be performed at proportionately lower fluxes. Thus, a 1000 mg sample irradiated at 10^{10} n/cm²/sec contains as much activity as a 1 mg sample irradiated at 10^{13} n/cm²/sec. Since the subcritical device discussed here develops 3.5×10^{10} n/cm²/sec, neutron activation analysis can be performed at the same level of accuracy as that of a reactor, if the sample size is expanded accordingly (see Figure 3.3).

The use of a cyclic activation analysis mode for increased sensitivity has also been

FIGURE 3.2. Pneumatic Sample Irradiation System for Neutron Multiplier Facility

FIGURE 3.3. Shown is a Spectrum of the 0.3 g Orchard Leaf Specimen Irradiated to a Fluence of 1×10^{17} Following a Decay Interval of 3 Days and an Analysis Time of 200 min on a Simple 25% Efficient Ge(Li) Diode. The rare earth spectra were obtained following radiochemical group separation. The spectra shown are that obtained for reactor irradiation. However, it is identical to that obtained from the subcritical facility operation when the subcritically irradiated sample was 20-fold larger, the irradiation time was twice as long, and the counting time was 5-fold longer.

studied. The sequence of a 10 sec irradiation, followed by a 1 sec decay, and a 10 sec count was repeated 20 times. Similarly, another sequence of a 100 sec irradiation, a 10 sec decay, and a 100 sec count was repeated 20 times. The elements Al, Cl, Cu, Na, Mg, K, Mn and Br were detected in bovine liver standard, while Al, Ti, V, Mn, Dy, Na, Mg, Sc, Ca and K were detected in geological standard BCR-1.

Cyclic activation analysis allowed these standards to be analyzed at accuracies which are close to those listed by the National Bureau of Standards and the United States Geological Survey.

Transuranium Element Measurement Techniques for High and Low Level Wastes Associated with Power Reactor Fuels Processes N. A. Wogman

As wastes are generated in light water reactor programs, or as anticipated in future breeder reactor programs of ERDA and the power industry, a variety of transuranium waste elements will require monitoring. One monitoring method which is being considered is the analysis of x-rays from elements decaying by alpha emission, and the identification of low energy photons from elements decaying by either alpha or beta emission. This type of instrumentation is required in the power reactor or breeder reactor fuel cycle for accountability purposes, hull monitoring, analysis of residual

solids or released gases, and, the identification of transuranium elements in high- and low-level waste streams. Some transuranium isotopes which can be identified in this manner are ^{237}Pu , ^{238}Pu , ^{239}Pu , ^{241}Am , ^{243}Am , and ^{242}Cm .

The low energy photons obtained indicate that ^{237}Pu (Figure 3.4) is most easily measured with its 101.1 keV photon. Plutonium-238 is most easily measured with its 43.5 and 99.7 keV photons. Plutonium-239 can be measured through its 98.5, 51.6 and 46.2 keV photons, or if ^{238}Pu is absent, from its 13.6 and 17.2 keV x-rays. Plutonium-237 and ^{241}Am decay to the same energy state of ^{237}Np resulting in the emission of a 59.6 keV photon. To measure ^{241}Am with a 59.6 keV photon, 101.1 keV ^{237}Pu peak must be used to determine the quantity of ^{237}Pu present and thus the amount of its contribution to the 59.6 keV peak area. Americium-243 is most easily measured with its 74.7 keV photon and ^{242}Cm is measured through its 44.1 keV photon, its 86.6 photon, or its 14.3 and 18.3 keV x-rays.

When low energy photon radiation is analyzed, a large area planar intrinsic Ge detector is the detector of choice, providing high resolution and low background. Its resolution must be better than 300 keV if x-ray photons are to be identified. This can be accomplished with planar intrinsic Ge detector sizes of 500 mm².

FIGURE 3.4. Low Energy Photon Spectrum of ^{237}Pu Observed with a Low Resolution Intrinsic Ge Detector

Use of X-Ray Spectrometry in Neutron Activation Analysis

K. K. Nielson, J. C. Laul and N. A. Wogman

A relatively large number of the radio-nuclides resulting from neutron activation of environmental samples decay with the emission of x-rays in addition to their more widely utilized gamma ray emissions. X-ray spectrometry with such samples has been avoided largely because of relatively poor detector resolutions and efficiencies below 100 keV with most Ge(Li) detectors, poor efficiencies above ~50 keV with most Si(Li) detectors, and attenuation of the relatively low energy x-rays by the sample material itself. The advent of the intrinsic Ge detector provides excellent resolution and efficiency in the 20-500 keV range and thus potentially solves the photon detection problem. In a preliminary study, we have examined the x-ray yields from selected nuclides relative to the corresponding gamma ray yields to evaluate the analytical potential of x-ray spectrometry of neutron activated samples.

Solutions containing rare earth group separations from a variety of neutron activated samples have been counted on both a Ge(Li) diode and an intrinsic Ge diode for comparing the gamma ray and x-ray counting methods. Net peak intensities from both methods were normalized at the 150 keV intensities to permit comparison of the relative sensitivities, as listed in Table 3.1. The greater relative efficiency of the intrinsic Ge diode for low energy photons results from its thinner photon window, and gives greater sensitivities for both x- and gamma rays in the low energy region (150 keV). The use of x-ray peaks offers a sensitivity advantage over use of the most intense gamma ray in the cases of several elements such as Nd, Sm, Eu, Ho, Yb, and Lu.

Similar comparisons have indicated that analysis of Ba by counting ^{131}Ba as separated by BaCrO_4 precipitation¹ can also be done more efficiently by counting the Cs K α x-ray peaks. Such applications of x-ray counting to biological samples has considerably reduced the necessary counting times for

TABLE 3.1. Comparison of Normalized Photopeak Intensities Using a Ge(Li) Diode and an Intrinsic Ge Diode on an Activated Rare Earth Solution

Nuclide	Ge(Li)		Intrinsic Ge		Ratio of Largest Peaks Int.Ge/Ge(Li)
	Energy (keV)	Intensity (c/min/ μ g)	Energy (keV)	Intensity (c/min/ μ g)	
^{140}La	487.	1.3	34.8 ^(a)	0.7	0.5
^{149}Nd			38.7 ^(a)	3.8	3.8
	156.	0.3	156.	0.3	
	114.3	1.0	114.3	1.6	
^{153}Sm			41.6 ^(a)	153.	4.6
	103.2	33.	103.2	82.	
^{152m}Eu			40.1 ^(a)	1950.	22.4
	842.	87.	121.8	326.	
^{166}Ho			49.2 ^(a)	1200.	7.3
	80.6	164.	80.6	720.	
^{171}Er			50.8 ^(a)	2.1	2.3
	308.	0.9	111.7	1.1	
^{177}Yb			54.2 ^(a)	5.3	4.1
	150.	1.3	150.	1.3	
^{176}Lu			55.8 ^(a)	24.	3.3
	88.4	7.3	88.4	20.	

(a)X-ray peaks

chemically separated samples and improved the corresponding detection limits. Many potential pollutant elements such as Hg, I, Sb, Sn, Cd, and Se are also subject to x-ray spectrometry following irradiation,² and may show sufficient x-ray intensities for similar advantages in analytical use.

In-Situ Activation and Photon Detection Techniques for Uranium Ore Evaluation R. L. Brodzinski and N. A. Wogman

Four different techniques have been evaluated for borehole analysis of U and Th ores. The methods involve the detection of fission product photons following ^{252}Cf activation, the detection of low-energy gamma-rays, the direct measurement of the 1001 keV photon from ^{243m}Pa , a progeny of ^{238}U , and isotopic excitation x-ray fluorescence spectroscopy.

Of the four assay procedures investigated, two were found applicable to the in-situ determination of low-grade U ore. The first is the borehole assay with the x-ray fluorescence spectrometer utilizing ^{57}Co isotopic excitation and an intrinsic Ge diode

detector. The second method is the direct detection of the nonfractionated daughter photons of U. The experimental procedures for each of these four methods are discussed separately below.

Detection of Fission Product Protons Following ^{252}Cf Activation

A 30 g sample of simulated ore containing 2% U_3O_8 was irradiated with 7 mg of ^{252}Cf in a water moderator. The short half-life fission products ^{90}Kr , ^{139}Xe , ^{140}Cs , and ^{144}La were analyzed with a 26% efficient Ge(Li) diode spectrometer. A similar experiment detected the fission product delayed neutrons with a 4-cm diameter BF_3 counter. For this sample size, 10 times as many events were observed with the gamma-ray detector system than with the neutron detector system. Further experiments in a field mock-up system containing 0.29% U ore demonstrated that the photons emitted from neutron activation of aluminum in the ore were sufficiently intense to obscure the photons of interest arising from the fission products of the U. Therefore, this technique is useful only for the analysis of high-grade ores, low-grade

ores which are low in Al content, or for monitoring, milling and fabrication process control.

Direct Detection of U and Th Gamma-Rays

Although U and Th decay primarily by alpha particle emission, they also emit a limited number of low energy photons. The predominant photon energies are 48 and 59 keV for U and Th, respectively. These energies are too low to allow a sufficiently large sample of U and Th to be analyzed in a field program. No statistically significant photopeak could be observed at either 48 or 59 keV from even high-grade ore in a 5-minute counting period.

Direct Detection of Uranium Daughter Photons

One progeny of U, which is virtually certain to be in equilibrium with uranium, ^{234}mPa , emits a 1001 keV photon. Although this photon occurs in only 0.6% of the U decays, it is relatively long-range and thus represents a reasonably large sample volume for analysis. A 0.029% U ore could be analyzed with a statistical uncertainty of 27% in a 1-minute counting period using a 26% efficient Ge(Li) diode. Although relatively long count periods are required to obtain

high precision in low-grade ore fields, a programmed system could be applied as a field unit to optimize scanning speed, such that any predetermined precision could be obtained in areas of varying ore concentration. This technique, although applicable for determination of U concentrations, is not applicable to the measurement of Th, since there are no high-energy gamma rays emitted in the Th decay chain from daughters having a negligible probability of being geologically fractionated.

Determination of Uranium and Thorium by X-ray Fluorescence Spectroscopy

Recent advances in state-of-the-art x-ray detector systems have allowed this technology to be considered for characterization of ore fields with in-situ measurement techniques. A 0.29% U ore and a 1% Th ore were analyzed using a 400-mm² x 5-mm thick intrinsic Ge detector with a 58 μCi ^{57}Co excitation source. The data illustrate that 0.01% U ore can be analyzed using a factor of 10 larger excitation source in 10 seconds with a statistical uncertainty of only $\pm 7.3\%$. The same grade of Th ore can be analyzed with an uncertainty of only $\pm 11\%$.

• ENVIRONMENTAL POLLUTION ANALYSIS - INSTRUMENTS AND METHODS DEVELOPMENT

Assessment of energy related pollutants at their sources and in effluents transported through the environment calls for ultrasensitive and reliable analytical instruments and methods. Analysis methods have been developed for measurement of the chemical forms and quantities of priority pollutant elements including: 1) As, Sb and Se in fresh, geo-thermal and sea waters by precipitation and x-ray fluorescence; 2) Hg in environmental waters by amalgamation and flameless atomic absorption; and 3) Cu, Pb and Cd in sea water by direct anodic stripping voltammetry using custom and commercial electrodes. New methods for x-ray fluorescence matrix corrections and data reduction also provide new capabilities for accurate multielement analyses of solid samples without requiring matching standards.

Analysis of Trace Elements in Sea Water by Anodic Stripping Voltammetry (ASV) K. H. Abe1 and E. A. Crecelius

Anodic stripping voltammetry (ASV) is an extremely sensitive electroanalytical technique which allows direct measurement of Cu, Pb, and Cd in natural waters at subpart per billion levels. Direct measurement, a distinct advantage over most other techniques which require a preconcentration step, coupled with relatively rapid sample analysis makes ASV attractive for environmental pollution studies.

During the past year, wax impregnated graphite (WIGE), pyrolytic carbon, and glassy carbon electrodes have been used in anodic stripping analysis. The WIGE and glassy carbon electrodes were commercially obtained while the pyrolytic carbon electrodes have been constructed on site. All three were found applicable in the subparts per billion range for copper and lead; however, electrode aging characteristics vary significantly.

Pyrolytic carbon and WIGE electrodes age or deteriorate much more rapidly with use than glassy carbon, although the electrode surface on the former two can be restored several times to near original behavior

by buffing or polishing. Effective lifetimes under our research conditions have been in the range of hours to days for these electrodes. The glassy carbon electrodes have shown much longer lifetimes (weeks to months), but, at present, we have been unable to restore the electrode surface as aging occurs.

Analyses of Pacific Northwest Coastal sea water using this technique indicate very low free ionic copper concentrations on the order of 20-100 ng/l. These analyses were performed at a pH of ~4.5 after removal of dissolved oxygen by CO₂. Total copper concentrations, determined after samples were exposed to ultraviolet light or ozone to release organically bound copper, have been found to be in the range of 100-200 ng/l. The copper concentrations found in this work are lower than the literature average for copper in sea water, 1-3 µg/l, but in general agreement with more recently published data from both the Atlantic and Pacific oceans.

Analysis of Mercury Species in Water C. L. Wilkerson and E. A. Crecelius

During recent studies of Hg in water, a procedure was successfully applied to

separate highly toxic methyl mercury (CH_3Hg^+) from inorganic Hg (II) ions. When applied to laboratory distilled water containing known amounts of CH_3Hg^+ and Hg^{++} ion, the procedure was found to provide effective Hg speciation analysis. This procedure will aid in identifying and measuring Hg species in environmental materials.

The procedure briefly consists of reducing dissolved Hg species to elemental Hg vapor (Hg^0) with stannous chloride (SnCl_2) and sodium borohydride (NaBH_4) as reducing agents. Reduced Hg^0 was subsequently removed from solution by aeration, amalgamated with gold, and finally measured by a flameless atomic absorption technique. The Hg^{++} ion was selectively reduced from a 50 ml water sample by adding 1 ml of a 20% SnCl_2 - 20% HCl solution. To determine the CH_3Hg^+ concentration of the test sample, a second 50 ml aliquot was reduced with 2 ml of a 2% NaBH_4 solution. This very strong reducing agent reduced both dissolved Hg species to Hg^0 ; the CH_3Hg^+ contribution was then found by difference.

The application of this two-step reducing procedure was simple, rapid, and was shown to be sensitive to 1-2 ng of Hg during a single determination. For analysis of natural waters containing numerous dissolved Hg species, the technique should provide effective differentiation between inorganic and organic Hg constituents. Future use of the procedure in our laboratory will yield valuable information about the chemistry of Hg in aqueous solutions.

Analysis of Arsenic, Antimony and Selenium in Solution by X-Ray Fluorescence of Ferric Precipitate E. A. Crecelius

The As, Sb and Se levels in natural waters usually range from <0.1 to >10 ppb. Concentrations >10 ppb are considered a potential hazard. The analytical methods that are currently used to measure these elements at natural levels are time consuming and expensive. Thus, a reliable, fast, inexpensive technique has been developed for the analysis of As, Sb^{+3} and Se^{+4} in natural water.

The technique consists of coprecipitating As, Sb^{+3} and Se^{+4} from solution with $\text{Fe}(\text{OH})_3$, then mounting the precipitate and quantifying the arsenic by x-ray fluorescence (XRF). The method has a detection limit of 3 ppb As, Sb^{+3} and Se^{+4} in 50 ml of water. In the procedure, 4 mg of Fe^{+3} in dilute HCl is added to a 50 ml sample of filtered water. The pH is adjusted to 4-5 using a few drops

of 20% NH_4OH . The $\text{Fe}(\text{OH})_3$ precipitate is filtered onto a 47-mm diameter, 0.4 μ -pore-size membrane filter. After drying, the precipitate is analyzed for As, Sb and Se by XRF. Care must be taken to correct for the Pb-L α counts that interfere with the As-K α line. Standards are prepared by spiking water samples that have already been precipitated and filtered. Blanks are prepared by precipitating $\text{Fe}(\text{OH})_3$ in water samples that have already been processed. Time required per sample is of the order of 60 min.

This technique has been applied to fresh water, sea water and geothermal water. The extraction efficiency of $\text{Fe}(\text{OH})_3$ for As^{+3} , As^{+5} , Sb^{+3} and Se^{+6} is over 95% in these waters.

Matrix Corrections for X-Ray Fluorescence Analysis Using Scattered X-Rays K. K. Nielson

Although x-ray fluorescence is perhaps the least expensive multielement analytical procedure for environmental studies, time consuming sample preparation and calibration procedures to avoid matrix effect errors have sometimes offset this advantage. Thin ($\sim 1 \text{ mg/cm}^2$) samples avoid these problems altogether, but environmental samples usually require considerable physical and chemical preparation to reduce them to a uniform thin geometry and have potential errors from chemical yield and contamination. A mathematical correction procedure has been developed³ to use the back-scattered exciting x-rays observed in the energy dispersive spectrum to compute corrections for matrix effects. The method thus permits simple pelletizing of most environmental samples and relies on a one-time thin sample calibration of the spectrometer.

Absorption coefficients for relatively thick (63 mg/cm^2) homogeneous samples are iteratively computed from the quantities of the heavy ($Z \geq 14$) elements measured from fluorescent x-ray peaks and from an estimated bulk light element composition measured from the scattered x-ray peaks. Intensities of the coherent and incoherent x-ray scatter peaks are corrected for absorption and for contributions from the observed heavy elements before being used for the light element estimate. Two representative light elements are selected from the corrected coherent/incoherent scatter intensity ratio and their masses are determined from the corrected scatter peak intensities. With the total sample mass thus defined, corrections for matrix absorption and enhancement due to secondary fluorescence are possible. Additional corrections

required for particulate samples can also be computed if an estimate of the particle size and density is available. Corrections are applied iteratively as illustrated in Figure 3.5 since they are interdependent and must converge to self-consistent values.

Relative precisions of the absorption corrections varied with each element from 0.5-2.0% in 15 repeated analyses of a single NBS standard orchard leaf pellet, and even better precisions appear possible.³ The accuracy of this method is illustrated by the data in Figure 3.6 for a BCR-1 rock sample. The magnitude of the various matrix corrections are also illustrated there.

This matrix correction procedure thus eliminates the calibration otherwise required for every sample type analyzed, and potentially simplifies sample preparation procedures. Matrix-corrected quantities of 24 elements can be derived from 1024 channels of raw data in 20-50 sec (5-15 iterations) using 24K,PDP-15 computer.

FIGURE 3.5. Computer Operation Flow-chart for Matrix Corrections for X-Ray Fluorescent Data

FIGURE 3.6. X-Ray Fluorescence Matrix Corrections for a Pelletized Rock Sample (USGS-BCR-1)

Evaluation of a Simple Method for X-Ray Peak Analysis K. K. Nielson

Integration of net peak areas in the digitized spectra resulting from x-ray fluorescence analysis of environmental samples is frequently complicated by overlapping photo-peaks in the spectra and by matrix effects. A modification⁵ of Covell's direct method⁶ for gamma ray peak analysis has been found to give excellent results in x-ray peak integration even in crowded spectra. The direct method defines background by linearly connecting the intensities at the integration window boundaries. By using a sufficiently narrow integration window, the resulting net peak area is a fixed function of the total net peak area and is independent of the intensity or slope of the linear background continuum.

This method has been evaluated for both systematic and random errors using single element spectra and spectra from repeated analyses of an NBS orchard leaf pellet. Systematic errors caused by peak overlap are compared in Figure 3.7 using conventional

FIGURE 3.7. Peak Overlap Errors (shaded areas) for a) Integration with Separately Determined Background, b) Covell Integration and Background Definition and c) Covell Integration of a Spectrum Containing Only the Interfering Element Peak

(a) and direct (b) peak analysis methods. As indicated, the magnitude and sign of the net overlap error depends on the widths and separation of the given peaks. It can be shown, however, that the net error indicated in Figure 3.7b is equal to that illustrated in Figure 3.7c for a single element spectrum, making overlap corrections for direct peak analysis possible by the usual alpha coefficient methods. The optimum integration window width must compromise between the good precision obtained with a wide window and the minimal peak overlap with a narrow one. Overlaps in environmental samples indicate that a width of approximately 1.4 FWHM is routinely practical.

Precision of direct net peak areas was found to improve significantly when the raw data was first smoothed once or twice using the five-point method of Savitzky and Golay.⁷ Repeated further smoothing gave little

improvement in precision but lowered peak areas by about 0.1% per smoothing in the test spectra where the peak FWHM varied from 7-12 channels. Seven and nine point smoothings were found to affect peak analysis identically to multiple five-point smoothings. Data smoothing offsets most of the increase in peak area uncertainty which arises from using the direct integration method.

By avoiding separate background estimates, this method provides significant advantages in both simplicity and accuracy in energy dispersive x-ray fluorescence spectral analysis. The method is excellent for completely automatic data reduction and could be equally advantageous in other energy dispersive systems such as particle induced x-ray emission.

• OIL SHALE AND TAR SAND RESEARCH

During the development of new energy technologies, concern has arisen as to their potential effects on human health and the environment. In order to identify these potential effects early in process development, it is necessary to chemically and physically characterize the effluents from various pilot operations. Because of the complex nature of the samples, new sampling and analytical techniques need to be developed. In this section new or improved techniques for both organic and inorganic analysis are described along with applications to effluents from coal conversion, oil shale retorting and geothermal pilot operations. Also described is a program for providing relatively homogeneous and well characterized research materials from oil shale and coal conversion pilot plants for biological and environmental studies and interlaboratory comparison.

Gas Chromatography/Mass Spectrographic Analysis of Shale Oil Fractions

P. W. Ryan

Characterization of organic compounds and compound classes in shale oil and other shale materials is an important part of the program of environmental health and oil shale studies. The very complex nature of shale oil, which results from the pyrolysis of oil shale kerogen, presents a considerable challenge to the organic analyst who must develop new methods to cope with this problem. A technique for identifying less abundant but important components in shale oil fractions is described below.

Following separation of shale oil into the acid, basic, neutral and PNA fractions (as outlined in Figures 3.10 and 3.11, page 72) each fraction is subjected to GC/MS analysis. Conventional GC/MS analysis consists basically of recording mass spectra of components as they elute from the GC column. These spectra are then compared to a reference library in order to identify the components. In relatively simple cases--for example the acidic fraction of shale

oil--this technique can establish the chemical identity of almost all chromatographable components.

The extreme complexity of all other fractions, however, calls for more sophisticated techniques. A chromatogram of the neutral fraction, which makes up some 80% of the oil, is dominated by a series of normal paraffins intermingled with a variety of branched paraffins and olefins. This entire collection of major peaks is superimposed on an "envelope" composed of hundreds or thousands of unresolved minor components, among which are many of the oxygen, sulfur, and nitrogen compounds of particular importance to the toxicologist and the process engineer. Under conventional conditions of electron impact ionization (EI), the spectra of minor components are effectively masked under fragments contributed by the major components. At the same time, a large background interference from the "envelope" precludes unambiguous mass spectral identification of the predominant hydrocarbons.

The difficulty has been attacked by employing several variations of chemical

ionization (CI) mass spectrometry, in which ionization is achieved by means of chemical reactions between the eluting substance and a reagent ion prepared in the mass spectrometer ion source. When reagent ions are prepared from methane, the hydrocarbons yield very simple, characteristic spectra such that the superimposed envelope contributions no longer cause problems in interpretation. The reagent ions prepared from isobutane or water lead to spectra similar to those from methane, but they are quite inefficient at producing ions from paraffinic molecules. As a result, the nonparaffinic compounds contribute 80 or 90% of the total ion current and the paraffin masking of their spectra is minimized. By going even farther and using ammonia to prepare reagent ions, the hydrocarbon spectra are entirely eliminated and the major peaks in the chromatogram are due to components previously obscured as part of the envelope. Many of these new major peaks are the oxygen, nitrogen and sulphur compounds, which are important to identify.

In summary, it has been demonstrated that, even in the case of an extremely complex system where the chemical and chromatographic separations are inadequate for mass spectral analysis by conventional means, the application of a sequence of chemical ionization techniques can provide a great deal of information about all major components and many minor ones that would not be available otherwise. Work continues on interpretation of the CI data and on the search for CI reagents that will bring out even more of the minor constituents.

Characterization of Products, Effluents and Wastes from Oil Shale Retort Pilot Plants

J. S. Fruchter, M. R. Petersen and J. C. Lau

In-situ and above ground technologies are being investigated to determine their feasibility for extracting liquid petroleum products from oil shale. The objective of the work reported here is to characterize products, effluents, and wastes from certain processes to support environmental and biological studies on those materials. The characterization reported here has been conducted on samples obtained from the simulated in-situ retorts of the Laramie Energy Research Center (LERC). We are grateful to LERC personnel for their cooperation in providing samples for analysis.

During the first year of this project, we have determined inorganic elements and their chemical forms in samples of raw shale oil,

retort water, gaseous emissions, and raw and spent shale. In addition, we have determined organic compounds in crude shale oil fractions and in the gaseous emissions. Two samples of oil shale, a sample of crude shale oil, a sample of process water, and several samples of the gaseous effluents were examined.

These initial inorganic element and speciation measurements indicate measurable amounts of the heavy elements Hg, Ag, Zn, and Se in crude shale oil, in process water, and in gas streams. In addition, the crude oil contains measurable amounts of Co, and the process water contains measurable Co, Br, Sb, and U. The data for the crude oil and process water are presented in Table 3.2. When the abundances of trace metals in raw oil shale are normalized to average crustal abundances, one finds that raw oil shale is enriched by the following factors: As(45), Sb(20), Se(86), U(3.5), Pb(3), and Hg(2.0) (see Table 3.3).

Raw shale oil samples have been separated into four organic fractions: neutral, polynuclear aromatics, acidic, and basic. The neutral fraction is composed largely of alkanes and alkenes. Although the polynuclear aromatic fraction has (see Figure 3.8) numerous aromatic hydrocarbons, it contains a surprising number of indoles. Identification of some of the compounds shown in this figure are based solely on mass spectrometry data and are subject to verification using gas chromatography retention time data. Numerous alkyl substituted indoles and carbazoles present in these fractions are indicative of the higher heteroatom content of shale oil. Higher numbers of the polycyclic compounds have been detected using selective ion monitoring including the benzopyrenes which are present in the ppm (10^{-6}) concentration range. The acidic fraction contains essentially all the isomeric forms of substituted phenols up to C₅-phenols. Some naphthols appear to be present. Further work using gas chromatography/mass spectrometry has shown that the basic fraction consists mainly of alkyl substituted pyridines, quinolines, and acridines.

Table 3.4 gives the chemical and physical forms of arsenic, mercury, iron, zinc and chromium in gaseous effluents in samples from a run of the 10-ton research retort at Laramie, both before and after the off-gas burner, which serves as an air emission control device for organic materials at this test facility. Preliminary speciation measurements indicate that most of the arsenic at this stage of the process is in the form

TABLE 3.2. Trace and Minor Elements in Oil Shale Retorting Materials in ppm

Element	Raw Oil Shale 15 gal/ton		Raw Oil Shale 40 gal/ton		Spent Oil Shale		Crude Shale Oil	Process Water	BCR ^(a)
	NAA	XRF	NAA + XRF		NAA	XRF	NAA	NAA	NAA
Na	16,100				23,400		19.4 ± 0.4	98 ± 1	23,500
Fe	20,700	20,700	17,400		42,100	47,000	30 ± 1	<1	95,900
Cr	30		21		52		0.04 ± 0.01	<0.02	15
Co	11		11		21.1		0.37 ± 0.02	0.65 ± 0.004	36
Ni		33	30			70			16
Sc	5.3		4.9		9.4		<0.0002	0.0004 ± 0.0001	34
Ba	320		370		650		<0.014	0.13 ± 0.02	680
Sr	440	380	490		1120	1080	<0.090	0.150 ± 0.05	320
La	15.9		16.2		34		0.0009	0.0017	24.6
Ce	31		30		62		<0.009	0.100	52
Pr	3.9				7.5		<0.0013	<0.0006	7.2
Nd	15				30		<10	0.055	30.3
Sm	2.4				4.90		0.00009	0.00031	6.3
Eu	0.43		0.45		0.82		<0.0002	0.00029	1.95
Gd	1.9				3.3		<0.00065	0.02	6.90
Tb	0.26				0.51		0.00006	0.0011	1.01
Ho	0.33				0.78		<0.0002	0.00008	1.26
Er	1.0				2.0		<0.008	<0.0015	3.4
Tm	0.14				0.36		0.00043	0.003	0.66
Yb	0.87		0.8		1.8		<0.0003	0.00036	3.38
Lu	0.140		0.18		0.34		<0.00003	0.000090	0.49
Hf	0.71		1.2		1.3		<0.004	<0.004	5.0
Ta	0.53		0.44		0.8				0.90
Th	4.3		4.4		8.2				6.5
U	7.0		5.6		12.7		0.0049 ± 0.0007	0.35	1.7
Rb	66	71	63		130	149			53
Cs	5.2		5.2		8±		<0.002	0.007 ± 0.002	1.1
As	81	63	108		91±	92	5.00 ± 0.04	5.89 ± 0.04	0.70
Sb	3.5		3.6		3.4		0.008 ± 0.001	0.016 ± 0.002	0.69
Zn		136	100			125	2.70 ± 0.08	0.43 ± 0.04	130
Br							0.079 ± 0.008	0.28 ± 0.01	0.10
Se		4.3	6			3.6	0.86 ± 0.22	0.98 ± 0.76	
Hg	0.2		0.1		0.003		0.2 ± 0.03	0.39 ± 0.05	0.010
Ga		4.1	5			11			
Cu		72	56			133			
Pb		39	43			41			

Note: Where estimated precision is not shown in this table, see Table 3.6.

(a)U.S. Geological Survey Standard Basalt BCR-1.

TABLE 3.3. Trace Element Abundances--Raw Oil
Shale/Crustal Average

Fe, Sc, Cr, Co, Na, Th, Ba, RARE EARTHS, Ni, Ga, Sr,
Cu, Ta, Hf, K, Rb RATIO = 0.2 - 1.5

As	45	Pb	3
Sb	20	U	3.5
Zn	2	Cs	2.0
Se	86	Hg	2.0

FIGURE 3.8. Polycyclic Compounds in Crude Shale Oil

of arsine gas. After the gas has been passed through the offgas burner, the arsenic concentration is reduced, due to dilution with air. After the offgas burner, a large fraction of the arsenic is trapped on a nucleopore filter and appears to be in the form of small arsenic trioxide particles. The mercury is seen to be largely in the form of Hg⁰ plus dimethyl mercury. Similar data are available for iron, chromium, and zinc--all from the first transition series of the periodic table.

Analysis of the retort offgas before burning the organic constituents by GC/MS

shows mostly hydrocarbons. A sample GC/MS trace is shown in Figure 3.9. Saturated hydrocarbons, alkenes, and alkynes (in both aliphatic and cyclic forms) were present. In addition, aromatic compounds, mostly substituted benzenes, were detected. No heterocyclics were identified in the offgas during this preliminary analysis.

Currently we are analyzing in depth the four shale oil fractions for organic constituents on GC/MS and will quantitatively determine the major organic compounds. Table 3.5 shows a list of compounds qualitatively identified in the four fractions.

TABLE 3.4. Trace Elements and Species in Offgas from a Run of the LERC 10 Ton Research Oil Shale Retort

		Before Offgas Burner(a)	After Offgas Burner
Arsenic	Gaseous	15,000 ng/m ³	1,400 ng/m ³
	Particulate	400 ng/m ³	2,500 ng/m ³
Mercury	Particulate	150 ng/m ³	600 ng/m ³
	Hg ⁺⁺	1,400 ng/m ³	100 ng/m ³
	(CH ₃) ₂ Hg ⁺	800 ng/m ³	300 ng/m ³
	Hg ⁰ +(CH ₃) ₂ Hg	10 ng/m ³	900 ng/m ³
Iron	Gaseous	120,000 ng/m ³	40,000 ng/m ³
	Particulate	6,000 ng/m ³	150 ng/m ³
Chromium	Gaseous	90,000 ng/m ³	35,000 ng/m ³
	Particulate	2,000 ng/m ³	600 ng/m ³
Zinc	Gaseous	40,000 ng/m ³	15,000 ng/m ³
	Particulate	500 ng/m ³	150 ng/m ³

(a) Occurs mostly in the form of arsine (AsH₃)

FIGURE 3.9. Gaseous Organic Components from 10-Ton Retort

TABLE 3.5. Compounds Identified in Shale Oil by GC/MS

Neutral Compounds

N-Alkanes	Branched Alkenes
N-Alkenes	Alkylfurans
Cyclohexane	Alkylthiophenes
Alkylcyclohexanes	Pristane
Branched Alkanes	Phytane

Aromatic Compounds

Indene	Acenaphthene	Chrysene
Alkylindenes	Fluorene	Methylchrysenes
Naphthalene	Alkylfluorenes	Cholanthrene
Alkylanisole	Phenanthrene/Anthracene	Benzofluoranthenes
Biphenyl	Alkylphenanthrenes	Benzopyrenes
Acenaphthylene	Fluoranthene	
Alkyl-naphthalenes	Pyrene	

Acidic Compounds

Alkylphenols	Thionaphthols
Naphthol	Thiophenols
Alkyl-naphthols	

Basic Compounds

Pyridine	Alkylacridines
Alkylpyridines	Indole
Quinoline	Alkylindoles
Alkylquinolines	Carbazole
Acridine	Alkylcarbazoles

Similar separation and GC/MS studies are underway for bitumen samples extracted from a sample of tar sand obtained near Vernal, Utah. We are also analyzing the raw and spent shales, oil and process water for a number of additional trace elements by using radiochemical neutron activation.

Fossil Fuel Research Materials:Preparation and Documentation

J. S. Fruchter and M. R. Petersen

The objective of this program is to prepare research materials from fossil fuel production or conversion pilot plants to be used in health and environmental studies. In carrying out such studies, it is important that representative materials from those processes, including products, effluents, and wastes, be available and that their composition be established as thoroughly as possible. In this program, materials from the more promising pilot operations are: 1) obtained, 2) stored in a manner that minimizes degradation, and 3) aliquots made available to ERDA laboratories and others designated by ERDA to conduct biological, health effects, and environmental studies.

To date, our efforts have largely been directed towards acquisition of materials from pilot operations to serve as "Research Materials", together with the design and acquisition of storage and handling facilities. We have fractionated a sample of shale oil into four fractions as a preliminary research material and have supplied aliquots of the fractions to Pacific Northwest Laboratory (PNL) biologists, who have conducted preliminary mutagenicity tests on them. Characterization of the four fractions, using GC/MS and neutron activation, has also been initiated by our group.

For the purpose of preparing research materials, two barrels of raw shale oil were acquired from the 150-ton research retort at the Laramie Energy Research Center (LERC).

For storage and distribution of the reference research materials, we have considered a number of containers and storage procedures that should minimize degradation or contamination. Our plans are to collect samples in teflon-coated stainless steel barrels, transfer them to amber glass containers, and store them in a refrigerated facility maintained at -2°C under a nitrogen gas atmosphere.

In preparing the preliminary oil shale research material, a batch of shale oil from the 150-ton LERC retort was split into four fractions using the separations scheme depicted in Figure 3.10. The fractions obtained were acidic, neutral, basic, and polynuclear aromatic, plus a residual insoluble tar. The percentages of each of the fractions obtained from the shale oil are shown in Figure 3.11. We are proceeding with organic analysis, using principally the GC/MS, and with inorganic analysis, using neutron activation.

The research materials will provide a means to improve relevant biological and environmental studies by facilitating comparison of methods and data between the various laboratories that conduct such studies.

FIGURE 3.10. Separation Scheme

FIGURE 3.11. Composition of a Sample of Shale Oil (Run # 13 of LERC 150-Ton Retort)

Determination of Mercury in Coal and Oil Shale Materials

C. L. Wilkerson

In the application of coal and oil shale technologies, we anticipate that various forms of mercury (Hg) in amounts that are of interest from an environmental standpoint will be volatilized from raw coal and oil shale. To provide a basis for investigating the fate of this volatile trace element, a procedure has been developed to accurately determine Hg in a variety of coal and oil shale materials. The procedure has provided rapid analysis of high precision and has been applied successfully to the determination of total Hg in raw coal, solvent refined coal, coal mineral residue, oil shale, spent shale, and shale oil. The detection limit for determining Hg in 100 mg samples is 5-10 ppb as measured by flameless atomic absorption spectrometry (f.a.a.s.).

The procedure quantitatively separates Hg from 50-150 mg samples by a process of sample combustion and thermal decomposition. The separation train (Figure 3.12) channels Hg-free air to samples, which are subsequently heated to 950°C in an enveloping quartz tube. The high temperature and oxidizing conditions within the tube volatilize Hg from the sample matrix and an underlying 3-4 cm layer of gold-coated quartz beads serves to convert the evolved Hg to elemental mercury vapor (Hg⁰). To separate Hg⁰ from interfering organic vapors, the effluent sample gases are directed into an acid washed chromosorb-W column which selectively retains most of the organic vapors but passes Hg⁰. The Hg⁰ is finally collected by amalgamation with a column of gold-coated glass beads maintained at room temperatures.

Following the amalgamation step, the column containing the trapped Hg is detached from the separation train and assembled into a f.a.a.s. system. Here the amalgamated Hg is released by heating the gold-coated glass beads to 500°C in a N₂ gas stream. The Hg⁰ vapor is swept into a long pathlength gas absorption cell where it is measured by atomic absorption at 254 nm.

The effectiveness of the procedure was tested by determining Hg in NBS coal (S.R.M. #1632) and NBS orchard leaves (S.R.M. #1571). These standard reference materials provided known Hg concentrations in representative environmental matrices. The resulting analysis together with Hg analysis for selected coal and oil shale materials is given in Table 3.6. The data for the two standard reference materials are in reasonable agreement with NBS certified values.

FIGURE 3.12. Separation Train for Volatilizing Mercury from Sample Materials

TABLE 3.6. Determination of Hg in NBS Standards and Selected Coal and Oil Shale Materials

Material	Total Hg Found (ppb)	Mean & Estimated Analytical Error (ppb)	NBS (ppb) Certified Value
NBS Coal	93,92,93,95,90,97	93 $\pm$ 10	120 $\pm$ 20
NBS Orchard Leaves	154,168,164,174,147	161 $\pm$ 15	155 $\pm$ 15
Feed Coal	172,179,155,165,148	164 $\pm$ 20	
Solvent Refined Coal	19,16,20	18 $\pm$ 3	
Coal Mineral Residue	<5,<5,<5	<5	
Oil Shale (1)	268,274,263	268 $\pm$ 20	
Oil Shale (2)	107,101,80,100,98,97	97 $\pm$ 10	
Spent Shale	19,12,13,14	15 $\pm$ 4	
Shale Oil	153,202,177,138,203	175 $\pm$ 30	

Multielement Analysis by Sequential Instrumental Neutron Activation

J. C. Laul, L. A. Rancitelli and J. S. Fruchter

In geological and environmental studies dealing with nuclear, fossil, and geothermal energy; neutron activation analysis (NAA) is being widely used for nondestructive multielement analysis. With the recent developments in high-resolution and high-efficiency Ge(Li) detectors, and coincidence-noncoincidence Ge(Li) systems, the NAA-gamma spectrometry method has become a powerful multielement technique because of its high-precision sensitivity and freedom from matrix effects. The basic criteria for determining multielements by sequential instrumental neutron activation analysis (INAA) are: 1) irradiation times; 2) decay interval prior to counting, 3) half-life and gamma-ray energy of a radionuclide, 4) the resolution and efficiency of Ge(Li) detectors.

Our sequential INAA, which has been revised and updated to permit analysis of fossil fuels and wastes, consists of two irradiation periods and four counting intervals. This enables us to determine about 30 elements in an aliquot. Table 3.7 lists the parameters, decay intervals and the isotopes observed in our procedure. Samples are irradiated at the Hanford N reactor or the TRIGA-III reactor at Washington State University (WSU). The irradiated samples are counted at an appropriate geometry on a 130 cc Ge(Li) diode (FWHM 1.8 keV for 1332 keV ^{60}Co) coupled to a 2048 channel analyzer. An example of the INAA using the WSU reactor is presented below:

Irradiation I: Samples and standards are individually irradiated at a neutron flux of 6×10^{12} n/cm²/sec for 5 min in the "rabbit" pneumatic facility at WSU. After the irradiation, the samples are allowed to decay for 15 min before they are counted on the Ge(Li) system for 5 min each. The elements Ti, Mg, V, Al, and Ca are measured in this count. Following this counting, the samples are allowed to decay for 3-5 hr to let the short-lived isotopes decay completely, and the samples are again counted on the Ge(Li) system for 15 min each. The elements Dy, Mn, and Na are measured in the second counting.

Irradiation II: Samples and standards are irradiated in a thermal neutron fluence of 1×10^{17} n/cm² in a rotating rack of the WSU reactor. After 5-7 days decay interval, the samples are counted for 30-100 min on the Ge(Li) system. Figure 3.13 shows a typical spectrum of the USGS BCR-1 rock sample counted for 30 min after a 7-day decay interval. There are, however, many isotopes identified in the spectrum. Only short and medium-lived isotopes of the elements Sm, Eu, Lu, Yb, Ba, Nd, La, Na, and K are measured at this time. The element Na measured also in the rabbit run provides an additional cross-check with the Na value obtained in this count.

After the completion of the first count, the samples are allowed to decay for another 40-50 days to let the short and medium-lived activities decay. The samples are then counted for 100-1000 min on the Ge(Li) detector system. The lower part of Figure 3.13 shows a spectrum of the BCR-1 sample counted

TABLE 3.7. Parameters and Decay Intervals for Instrumental Neutron Activation

Parameters	{ Neutron Flux = 6×10^{12} n/cm ² /sec	
	{ Irradiation I = 5 min	
	{ Irradiation II = 6 hr	
Decay Interval	Isotopes Observed	
15 min	^{51}Ti , ^{27}Mg , ^{52}V , ^{28}Al , ^{49}Ca	
3 - 5 hr	^{165}Dy , ^{56}Mn , ^{24}Na	
5 - 7 days	^{153}Sm , ^{152}Eu , ^{177}Lu , ^{175}Yb , ^{131}Ba , ^{147}Nd , ^{140}La , ^{24}Na , ^{42}K	
40 - 50 days	^{182}Ta , ^{152}Eu , ^{141}Ce , ^{160}Tb , $^{223}\text{Pa(Th)}$, ^{51}Cr , ^{181}Hf , ^{85}Sr , ^{95}Zr , ^{134}Cs , $^{58}\text{Co(Ni)}$, ^{46}Sc , ^{86}Rb , ^{59}Fe , ^{65}Zn , ^{60}Co , ^{124}Sb

FIGURE 3.13. Instrumental Neutron Activation Gamma-Ray Spectra

for 100 min after 40 days decay period. Sixteen elements (Ta, Eu, Ce, Tb, Th, Cr, Hf, Ba, Sr, Cs, Sc, Rb, Fe, Zn, Co, and Sb) corresponding to the isotopes listed in Table 3.7 are measured in this count. The photopeaks in the gamma ray spectra for elements Cr, Ba, Sr, Zr, Ni, Rb, Zn, and Sb are small relative to the Compton continuum and therefore have a large uncertainty, especially when they are present at low levels. The samples are therefore also counted on our anti-coincidence shielded Ge(Li) system which provides both coincidence and noncoincidence spectra.

The samples are counted for 30-600 min on this coincidence-noncoincidence Ge(Li) system. The systematics of this setup are that when an isotope emits two or more gamma-rays in cascade, and if they are simultaneously detected by the surrounding phosphor scintillator and the Ge(Li) diode, the coincidence events are stored in one half of the 4096 channel memory, while the single gamma-ray events are stored in the second half of the memory. Figure 3.14 displays spectra of coincidence and noncoincidence of the geological BCR-1 sample. The great advantage lies in the noncoincidence spectrum due to the fact that the Compton in the noncoincidence mode relative to the coincidence mode is reduced by an order of magnitude for low and medium gamma-ray energies. The peak to Compton ratios and sensitivities for elements Cr, Ba, Sr, Zr, Ni, Rb, Zn, and Sb in the noncoincidence spectrum are thus greatly increased. The 1116 keV peak of the Zn is easily measured by the reduced Compton edge of the 1121 keV peak of ^{46}Sc in noncoincidence. The elements Ni and Zr previously barely observed in our normal Ge(Li) counting are easily measurable in noncoincidence counting. Overall, the accuracy and relative precision for these elements are improved by a factor of 10 by noncoincidence counting relative to the normal Ge(Li) counting.

The estimated errors due to counting statistics based on BCR-1 are: ± 1 to 3% for Al, Fe, Mn, Na, Sc, V, Co, Zn, Rb, Ba, Sr, La, Sm, Eu, Yb, Lu, and Hf; $\pm 5\%$ for Ti, Ca, K, Cs, Dy, Ta, and Th; and ± 5 to 10% for Mg, Cr, Ni, Sb, Ce, Nd, Tb, and Zr. Our sequential INAA procedure has been tested on several replicates of geological and biological standards. Our results in general agree very well with the literature values.

Analysis of Coal Conversion and Oil Shale Retorting Materials by Radiochemical Neutron Activation Analysis J. C. Laul and J. S. Fruchter

A radiochemical separations scheme for neutron activation products from 25 trace elements; Ag, Au, Ba(U), Cd, Co(Ni), Cs, In, Rb, REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb and Lu), Sb, Se, Sr, Tl, and Zn, has been developed for coal conversion and oil shale retorting materials. This technique is ideal for these very complex materials, since it is virtually free from matrix effects. The concentrations of these elements in the samples are measured by a group separation; whereas the other elements are analyzed by other separations. The scheme has been successfully tested on a USGS standard BCR-1 sample, and the precision for most of the trace elements lies between 2 and 10%.

A sample aliquot of 0.2 - 0.4 g is sealed in a 2/5 dram polyethylene vial, and the 2/5 dram vial is placed in a 2-dram polyethylene vial and heat sealed. The samples and standards are irradiated together at a neutron flux of 6×10^{12} n/cm²/sec for 7 hr in a rotating rack of the Washington State University (WSU) reactor. After a decay period of 2 to 3 days, the sample is transferred into a Ni crucible in which the inactive carriers (1 - 10 mg/ml) in appropriate amounts for the above elements were already dried. The sample is fused with an appropriately 1g NaOH - 5 g Na₂O₂ mixture to a clear melt. The melt is cooled, the fused mass decomposed with H₂O in a beaker, and 10 ml of 10% Na₂S solution added. In the case of a liquid sample, the irradiated sample is transferred into a beaker containing the carriers and digested with concentrated HNO₃ for several hours. The nitrate ions are then removed on heating by several repeated additions of concentrated HCl. The solution is made basic with NaOH and 10 ml of 10% Na₂S solution is added. The hydroxide and sulfide precipitate contained Ag, Au, Ba(U), Cd, Co(Ni), In, Sr, REE, Tl, and Zn, whereas the supernate contained Cs, Rb, Sb, and Se. Figure 3.15 shows a flow scheme of the separations indicating the element or elements in different fractions.

Precipitate: The bulk of the precipitate is dissolved in concentrated HNO₃. The nitrate ions are removed on heating with

(Ag, Au, Ba(U), Cd, Co(Ni), Cs, In, Rb,
REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho,
Tm, Yb and Lu), Sb, Se, Sr, Tl, Zn)

FLOW SCHEME

FIGURE 3.15. Radiochemical Separations Flow Chart

repeated additions of concentrated HCl, and the solution is finally made up in 1M HCl. The Ag along with Ba and Sr remain in the precipitate and the solution is filtered onto a pre-equilibrated anion-exchange column (Bio-Rad Ag 1-X10 resin, 100-200 mesh). The eluant contains Co, In, and REE. The column is further treated with 0.1M HCl to elute Zn, 0.00M HCl to elute Cd, and 1M $\text{H}_2\text{SO}_4(\text{SO}_2)$ to elute Tl. During the Tl elution, gold is reduced to metal by sulfur dioxide. The column is treated with aqua regia to redissolve gold, and the column is washed with H_2O and then gold is eluted with 0.1M HCl - 0.1M thiourea.

Supernate: To the supernate from the hydroxide and sulfide precipitate, cadmium sulfate is added to remove any excess sulfide and the CdS precipitate is discarded. The supernate from the CdS precipitate is acidified with H_2SO_4 and $\text{Fe}(\text{OH})_3$ scavenging is performed with 6M NaOH. The $\text{Fe}(\text{OH})_3$ precipitate contains Sb. The supernate from the $\text{Fe}(\text{OH})_3$ is adjusted to pH ~1 with H_2SO_4 , and terphenyl boron is added to precipitate Rb and Cs. The supernate containing Se from the Rb and Cs precipitate is adjusted to 1M H_2SO_4 , and Se is reduced to metal on heating with hydrazine hydrochloride.

Following the crude separation, elements are further radio-chemically purified by their standard radiochemical procedures. Based on their nuclear properties including half-lives and gamma-energies, the radionuclides are counted on NaI(Tl), Ge(Li) and beta-counting equipment. Table 3.8 gives a brief summary of the radionuclides, half-lives, gamma-energies, and counting equipment used in our chemistry procedure.

The REE group separation: The fraction containing the REE, Co(Ni), and In is treated with excess NH_4OH to precipitate In and REE as hydroxide; whereas Co is complexed with NH_4OH and remains in solution. The hydroxide precipitate of In and REE is then dissolved in HCl, and the REE is precipitated with excess 6M NaOH while In forms a complex and remains in solution. The group $\text{REE}(\text{OH})_3$ is next dissolved in HCl and precipitated as fluoride with NH_4HF_2 and HF. The REE fluoride is dissolved in HNO_3 and H_3BO_3 and precipitated as $\text{REE}(\text{OH})_3$ with NH_4OH . The fluoride and hydroxide cycle is repeated three times to ensure radiochemical purity.

The REE group aliquot is counted on our Ge(Li) system. Figure 3.16 displays the REE spectra of the geological BCR-1 standard counted after a 3 day interval. Essentially, 12 REE elements were measured in one count. The 1576 keV peak of ^{142}Pr is not shown in

the spectra. After a decay of 20-30 days, the sample is again counted to optimize the detection sensitivities for some elements. Chemical yields are determined by reirradiating the sample aliquots for 1 min in the "rabbit" pneumatic facility of the WSU reactor.

Measurement of Toxic Materials in Geothermal Fluids

J. S. Fruchter, D. E. Robertson and J. D. Ludwick

The objective of this work is to characterize the heavy metal and noxious gas emissions from the geothermal steam wells at Raft River, Idaho. Although many people consider geothermal steam to be a nonpolluting energy source, in fact, many geothermal plants have been found to emit heavy metals and noxious gases at rates that are comparable to emissions from coal-fired plants. Although there are no other environmental impacts, such as from coal mining and transportation, emissions from a geothermal plant may be more serious because the plant must be located near the wells leaving little flexibility in selection of the site. Consequently, it is desirable to begin assessment of potential environmental impact as early as possible. Each location must be assessed individually, since very large differences in emission levels have been noted previously at different geothermal areas. The Raft River site is particularly important since ERDA plans to construct a pilot plant at this location during the next 2 years.

During this past year, a sampling trip was made to the Raft River site using Radiological Sciences' mobile geothermal laboratory. Onsite measurements were made of mercury, hydrogen sulfide, ammonia, fluoride, Eh and pH in samples of brine, condensed steam, and noncondensable gasses (See Table 3.9). Measurements of arsenic species were made on returning to Richland. The heavy metals mercury and arsenic, and the gases hydrogen sulfide and ammonia were found to be quite low, about a factor of 100 lower than our group measured at similar geothermal wells at Cerro Prieto, Mexico. Arsenic at Raft River is mostly in the +5 state. Fluoride, on the other hand, was a factor of 5 higher than found at Cerro Prieto. If other heavy metals in the Raft River fluids are also low it may be that fluoride will be the only potentially harmful effluent at this site. The two orders of magnitude difference in heavy metals and noxious gases between Cerro Prieto and Raft River underscore the need to evaluate each geothermal prospect on an individual basis rather than attempting to generalize.

TABLE 3.8. Table of Radionuclides Via RNAA

Isotope	t(1/2)	γ Energy (keV)	Counting
Ag-110m	255 d	658	NaI(Tl)
Au-198	64.5 h	412	NaI(Tl)
Ba-131	11.6 d	122, 216	Ge(Li)
Ba-140	12.8 d	537	Ge(Li)
La-140 for U	40.2 h	1596	Ge(Li)
Cd-115	53.5 h	335(In ^{115m})	NaI(Tl)
Co-60	5.26 y	1173, 1132	Ge(Li)
Co-58 for Ni	71 d	811	Ge(Li)
Cs-134	2.05 y	605, 796	Ge(Li)
Rb-86	18.7 d	1078	Ge(Li)
In-114m	50 d	192	NaI(Tl)
Sb-124	60.3 d	603	NaI(Tl)
Se-75	120 d	136, 265	NaI(Tl)
Sr-85	64 d	514	Ge(Li)
Tl-204	3.8 y	--	β Counting (Bkg 1.0 cpm)
Zn-65	245 d	1115	NaI(Tl)

Note: Precision by RNAA: 2-10% depending on activity.

FIGURE 3.16. The REE Group Spectrum of BCR Sample

TABLE 3.9. Trace Constituents in Geothermal Effluents
from the Raft River ERDA Site

	Noncondensable Gas	Steam Condensate	Brine
H ₂ S	215 ppm	0.66 ppm	0.1 ppm
Hg	39 ng/l	124; 128 ng/l (a) 106 ng/l (b)	8; 35 ng/l
As	--	800 ng/l As ⁺³ 11,400 ng/l As ⁺⁵	2,800 ng/l As ⁺³ 24,900 ng/l As ⁺⁵
F ⁻	--	0.04 ppm	9.8 ppm
NH ₄ ⁺	--	1.9 ppm	0.29 ppm
Eh	--	+ 50 m.V. @ 30°C	+ 105 m.V. @ 30°C
pH	--	6.0 @ 24°C	8.6 @ 30°C

Steam/brine = 1/14 by weight

Noncondensable gas/steam = 0.02% by volume at STP

(a) Hot oxidized

(b) Untreated

• DOSIMETRY OF INTERNAL EMITTERS

This program is generally aimed at providing dosimetric guidance and support to radiobiology studies at Pacific Northwest Laboratory (PNL). In particular, the program includes considerations of dosimetric design of experiments; materials; theoretical and experimental dosimetry of various tissues and eventual relating of dosimetry data to observed biologic effects. Organ and whole-body doses were calculated and measured in experiments aimed at elucidating the dose-effect relationships from exposure to ^{85}Kr gas, $^{239}\text{Pu}(\text{NO}_3)_4$ aerosols and cervical implants of ^{252}Cf and ^{226}Ra . Dosimetry relating acute lethality for rodent and beagle dog ingestion of insoluble beta emitters is included for a variety of beta emitters.

Dose to G.I. Tract from Ingested Insoluble Beta Emitters

F. T. Cross and G. W. R. Endres

Development of methods for improving the dose to the crypt cells in the G.I. tract from the ingestion of insoluble beta emitters was continued. The major portion of this data and all the methodology were reported in the 1975 Annual Report (BNWL-2000, PT4). The additional experiments included exposing the animals to mixtures of radioisotopes to more closely simulate the energy mix of the effluent of a reactor catastrophe. These experiments verified the previously derived LD_{50} values for a spectrum of beta energies based mainly on the results of exposure to ^{106}Ru - ^{106}Rh . Although Tables 3.10 and 3.11 cannot be considered precise guidance of lethal levels, they do appear to predict the experimental data quite well. The crypt cells in beagle dogs were found to lie, on the average, at about 0.0750 cm depth and in rats at about 0.0175 cm depth. Lethality predictions are based on damage to these cells. The other depths are included to show how the required amount of radioisotope to produce acute lethality varies with depth of crypt cell.

Dosimetric guidance was provided to many other radiobiology studies at PNL. In particular, there is an ongoing calculational-experimental measurement of organ and whole-body dose to rodent and beagle dog from inhaled ^{85}Kr gas in experiments to elucidate the biologic effects of potential gaseous reactor effluents. Dose and organ burden modeling along ICRP-2 methodology is provided to the $^{239}\text{Pu}(\text{NO}_3)_4$ experiments with beagle dogs as a distinct and additional effort for intercomparison with a separate analog modeling methodology. Considerable effort was applied to calculating and measuring the combined neutron and gamma doses to swine ureter, bladder, colon, and other organs from implanted cervical sources of ^{252}Cf and ^{226}Ra . The neutron RBE for early changes in the tissues at risk in the treatment of cervical cancer was determined to lie between 6.2 and 6.8 whereas the RBE for delayed effects appears to be somewhat decreased, most likely a result of tissue repair. These studies continue in order to more accurately fix the neutron RBE for delayed effects and to determine the limitations of implanted neutron sources for treating cervical cancer. Such studies and others will be reported in greater detail as the data develops.

TABLE 3.10. Dose Extrapolation for Dog Colon
 $\sim LD_{50}$ (mCi/kg)(a)

Radioisotope	Depth, cm			
	0	0.0175	0.0500	0.0750
$^{106}\text{Ru}-^{106}\text{Rh}$	3.5	3.5	3.5	3.5
^{90}Y	4.9	5.3	5.7	6.0
^{32}P	6.5	7.3	8.7	9.8
^{210}Bi	11	13	28	31
^{204}Tl	17	32	69	1.3×10^2
^{90}Sr	22	51	1.8×10^2	6.0×10^2
^{212}Pb	40	2.2×10^2	2.3×10^3	$\sim 5 \times 10^4$
^{103}Ru	66	1.6×10^3	$\sim 1 \times 10^6$	$\sim 2 \times 10^8$
^{147}Pm	67	2.0×10^3	$>10^7$	--

(a) Based on $^{106}\text{Ru}-^{106}\text{Rh}$ experiments.

TABLE 3.11. Dose Extrapolation for Rat Cecum
 $\sim^{10}\text{LD}_{50}$ (mCi/kg)(a)

Radioisotope	Depth, cm	
	0	0.0175
$^{106}\text{Ru}-^{106}\text{Rh}$	9.0	9.0
^{90}Y	13	14
^{32}P	17	19
^{210}Bi	28	39
^{204}Tl	45	81
^{90}Sr	55	1.3×10^2
^{212}Pb	1.0×10^2	5.7×10^2
^{103}Ru	1.7×10^2	4.1×10^3
^{147}Pm	1.7×10^2	5.1×10^3

(a) Based on $^{106}\text{Ru}-^{106}\text{Rh}$ experiments.

• ANALYTICAL TECHNIQUES FOR ^{99}Tc MEASUREMENT IN ENVIRONMENTAL SAMPLES

A highly sensitive mass spectrometric technique is being developed for measurement of ^{99}Tc in environmental samples. The feasibility of this approach has been demonstrated, and necessary refinements are now being made to the radiochemical and mass spectrometric procedures. Interfacing of the mass spectrometer to a highly flexible and sophisticated PDP-11 based computer system has been accomplished. It is anticipated that measurements of ^{99}Tc at the picogram or subpicogram level will be possible by this technique.

Ultrasensitive Measurement of ^{99}Tc by Mass Spectrometry J. H. Kaye

From an environmental and hazard viewpoint technetium-99 is one of the most troublesome radionuclides produced through nuclear fission. This is due to the long half-life (2.13×10^5 years), the volatile nature of the heptoxide, the mobility of the pertechnetate ion in aqueous solution, the high fission yield (over 6%) and the affinity of several organs of the human body for this element. Furthermore, technetium is almost impossible to detect at very low levels by direct counting methods since its half-life is long and it emits only low-energy beta radiation. The purpose of this study is to develop, by means of mass spectrometry, much more sensitive methods for its detection than are presently available. Currently planned ecological studies within existing DBER programs are awaiting development of the ^{99}Tc analytical procedures. Other programs (e.g., waste management, environmental monitoring) also require availability of a sensitive analysis method for ^{99}Tc .

The objective of this study is to develop an analytical technique which will permit detection of technetium-99 in the environment at a much lower level than is now possible. The basic feasibility of accomplishing this by means of mass spectrometry has been demonstrated and described in the

previous report (BNWL-2000, PT4, February 1976). Sensitivities as low as 10 femtograms (10^{-14} g) were reported for the case of ammonium pertechnetate in aqueous solution. We are currently working to achieve this same kind of sensitivity in environmental samples. This involves refinements to the radiochemical techniques and computerization of the mass spectrometer system so that optimum operation of the system may be realized.

Although the technetium separation scheme is basically the same as was outlined in the previous report, some important changes have been necessary to reduce interferences in the mass spectrometer measurements. The initial, simplest approach after chemical separation and purification of the technetium was its electroposition directly onto a mass spectrometer filament as TcO_2 , reduction with hydrogen to the metallic form, and direct analysis. Unfortunately, it has been found that considerable molybdenum codeposits with the TcO_2 during the electroposition step. To prevent interference of the mass-97 isotope of molybdenum with the ^{99}Tc tracer which we plan to add, it will probably be necessary to redissolve the TcO_2 deposit and do further chemistry to remove the molybdenum, and then load the final aqueous solution directly into the filament. Current work on this post-electroposition chemistry procedure with radioactive tracers of molybdenum and ruthenium indicate that high decontamination factors from both of these elements will be obtainable without serious reduction of radiochemical yield.

Irradiations of ^{96}Ru are being made in order to obtain ^{97}Tc for use as an isotopic tracer in mass spectrometric analyses of samples. The chemical separation techniques for recovery of technetium from ruthenium in high yield ($\geq 75\%$) have been worked out and will be used to prepare purified ^{97}Tc tracer.

A highly sophisticated PDP-11 based computer system has been successfully interfaced to the mass spectrometer. Important features of this system include a) 16K words of core memory, b) dual, 2 million word, removable cartridge disk drives for storage of programs and data, c) graphics terminal for communication with the system and on-line output of data and plots, d) DEC writer for hard copy output, e) GOULD line printer/plotter for rapid output of programs, plots and data, and f) a complete laboratory peripheral system. The latter system allows transfer of data directly from the mass spectrometer into computer core memory, and permits on-line display of the acquired data. It will also enable mass scans to be taken, and will allow rapid transfer of digital information from a 200-MHz scaler into computer memory.

Figure 3.17 shows a mass scan of a distilled water blank sample obtained with the total mass spectrometer/computer system. Figure 3.18 shows a spectrum covering the same mass range for a sample containing 100 femtograms of ^{99}Tc . Both scans were taken at a current through the sample filament of 4.2 amperes. The effectiveness of the mass spectrometer technique and of this system for measuring picogram and smaller amounts of ^{99}Tc is demonstrated in these figures.

Further work remains to be done to complete the development of the $^{97}\text{Tc}/^{99}\text{Tc}$ isotopic ratio technique. Further refinements to the chemical separation procedures need to be worked out, and some additional interfacing between the computer and the mass spectrometer will be required. It is anticipated that a usable analytical procedure for analysis of ^{99}Tc at the picogram level or below can be established.

FIGURE 3.17. Mass Scan of Distilled Water Blank

FIGURE 3.18. Mass Scan of 100 Femtograms of ^{99}Tc

• TRACE CONSTITUENT ANALYSIS BY LASER EXCITATION

A high resolution dye laser system has been constructed and used to investigate the optical excitation and fluorescence analysis of xenon gas. A two photon excitation to the 1D_2 state has been observed via the ensuing fluorescence to the intermediate 3P_2 state. Theoretical calculations show that the use of counterpropagating beams to remove the Doppler effect should allow isotopically selective analysis.

Analysis of Trace Constituents by Laser Excitation

B. A. Bushaw and T. J. Whitaker

Lasers are being used today in an ever-widening field of endeavors. The high spectral irradiance and resolution achieved by lasers allow efficient, selective excitation of particular isotopic species. This may be followed by ionization, dissociation, chemical reaction, or other means to separate the excited atom or molecule. By monitoring the number of excited species, a very sensitive analytical technique may be developed. This program exploits the characteristics of lasers for two purposes: 1) to improve detection limits of existing analytical techniques which use optical excitation; and 2) to develop new analytical procedures for trace constituents which are impossible with conventional excitation sources.

One such unique process, for which a theoretical discussion was given in last year's report, is a fluorescence technique for real-time isotopically selective detection of krypton or xenon. The development of such a process is important since at present there are no real-time methods for monitoring the concentrations of noble gases. There is interest in being able to measure these trace constituents in the atmosphere, particularly ^{85}Kr , at very low concentrations. Under this program the described process has been observed experimentally in xenon.

Because the first excited states of krypton and xenon are very high in energy, a two-photon process is used to populate a 1D_2 state which then decays via fluorescence to a 3P_2 state. This fluorescence, at about 8400Å in xenon, may be monitored by conventional means. Basically, the spectrum of xenon is very similar to that of krypton; however, the xenon states are somewhat lower in energy than those of krypton. While a two-photon process is still required for excitation to the 1D_2 state of xenon, the lower energy of the transition simplifies much of the instrumentation.

Laser System

We have constructed a nitrogen laser pumped dye laser capable of resolution better than 0.001 angstrom. The tuning range is continuous from about 215-700 nm using various dyes and frequency doubling crystals. Power levels range from 1-20 kW in 5 nsec pulses with a repetition rate of 30 Hz.

Figure 3.19 shows a schematic of the high-resolution laser system consisting of a dye oscillator cavity and two single-pass amplifiers all pumped by a single 500 kW nitrogen laser. Wavelength tuning is accomplished with a diffraction grating in the oscillator cavity and two Fabry-Perot etalons, one at the input of each of the two amplifier cells.

FIGURE 3.19. High-Resolution Dye Laser System: The oscillator cavity is formed between a 9th order eschelle diffraction grating (1) and a 50% transmitting output mirror (4). The oscillator dye cell (3) is pumped by 10% of the N_2 laser beam extracted by a beam splitter (20) and focused by a cylindrical lens (23). A 20x telescope (2) is placed in the cavity between grating and dye cell to increase the effective resolution of the grating. The output of the laser cavity, with a bandwidth of 0.12Å, is passed through a pinhole spatial filter (5) to control the transverse mode structure and through a Glan-Thompson polarizing prism (6) resulting in a uniform Gaussian beam with linear polarization. The beam is then expanded and collimated with a 10x telescope (7) and directed to a Fabry-Perot etalon (8) which reduces the bandwidth to 0.012Å. The beam passed through the etalon is focused into the first amplifier cell (10) with another telescope (9). The amplifier cell is pumped by 30% of the N_2 laser output which has been passed through an optical delay line (21) to provide optimum coupling between the N_2 laser pulse and the oscillator pulse. The output of the first amplifier retains the 0.012Å bandwidth while providing an intensity gain of $\sim 10^3$. The output is passed through a second pinhole spatial filter (11) to control mode structure induced in the amplifier and through a system of telescopes (12,14) and a second Fabry-Perot interferometer (13) which reduces the laser bandwidth to 8×10^{-4} Å. Finally, the output of the second Fabry-Perot is amplified in another dye cell (15) pumped with the remaining 65% of the N_2 laser output, resulting in a near transform limited pulse with peak power of about 20 kW. The pulse is passed through a frequency doubling crystal (17) located at the center of a 5 cm confocal telescope (16,18) where, with a conversion efficiency of approximately 5%, the pulse is converted to its second harmonic in the ultraviolet. The ultraviolet is separated from the remaining fundamental with a set of fused silica dispersive prisms (19).

Experimental Work*

Scanning the laser slowly over the region at $1/2$ the energy of the 1D_2 transition in xenon, resulted in the predicted fluorescence signal. To unequivocally prove that we were really observing a simultaneous absorption of two photons, the oscillator bandwidth was broadened to produce a three frequency output corresponding to three successive orders

of the Fabry-Perot etalon. In the nonlinear doubling crystal, the three fundamental frequencies, ν , $\nu + 1$, and $\nu - 1$, were both mixed and doubled in frequency so that the result is five frequencies.

$$2\nu \pm N, N = 0, 1, 2.$$

Then, in the two photon absorption process, the xenon gas may absorb any combination of these five frequencies if the combination is in resonance with the transition. The resulting frequencies are:

$$4\nu \pm N, N = 0, 1, 2, 3, 4.$$

If ν is scanned, each of these nine combinations will come into resonance with the transition when

*This work was presented at the Annual Meeting of the Society of Photo-Optical Instrumentation Engineers, August 1976, San Diego, and reviewed in the October 1976 issue of Laser Focus.

$$4\nu \pm N = \nu_0, N = 1, 2, 3, 4$$

where ν_0 is the actual transition energy.

The experimental observation of the effect is shown in Figure 3.20. Due to asymmetry in the intensity of the three fundamental frequencies ($\nu + 1$ was less intense than $\nu - 1$) the +3 and +4 peaks were too weak to be observed.

Selective excitation with a single frequency laser line resulted in the spectrum shown in Figure 3.21. The peak is about 0.3 cm^{-1} full width at half maximum and the lack of a structure is due to Doppler broadening which causes the hyperfine levels to overlap. Also shown in Figure 3.21 is a theoretical calculation of the spectrum where the Doppler width has been convoluted onto the various hyperfine isotopic components. The use of counterpropagating beams of sufficiently narrow bandwidth will eliminate the Doppler effect, and is expected to reveal the hyperfine isotopic components.

The calculated spectrum of naturally occurring xenon isotopes within the frequency range of the 1D_2 level is shown in Figure 3.22. The even isotopes all merge together under the peak labeled 132, while the odd isotopes, having non-zero nuclear spin, split into hyperfine levels. The hyperfine splitting shown is calculated on a basis of the magnetic dipole interaction; electric quadrupole effects are neglected. Peak amplitudes are based upon the natural abundance of the particular isotope and calculated two-photon transition probabilities. The 0.005 cm^{-1} width of the peaks is imposed on the theoretical spectrum because the laser system is transform limited to about this value. Note that there is complete separation of the peaks and isotopically selective analysis should be possible when high-resolution Doppler cancelled spectra are obtained.

FIGURE 3.20. Excitation Spectrum of the 1D_2 State of Xenon Using a Three Frequency Laser Oscillator. The numbers assigned to the peaks are the n values as described in the text.

FIGURE 3.21. Theoretical and Experimental Excitation Spectra of the $1D_2$ State of Xenon Using a Single Frequency Laser. The transition is Doppler broadened.

FIGURE 3.22. Theoretical Spectrum of the $1D_2$ State of Xenon Without Doppler Broadening for a Mixture of Xenon Isotopes in Natural Abundances. Peaks are labeled by mass number and hyperfine F value for odd isotopes.

• APPLICATIONS OF HOLOGRAPHY

Holography using short laser pulses is being studied to determine its applicability to environmental applications. A Q-switched Korad 1500 ruby laser is being used for laboratory experiments to determine spatial and temporal resolving capability. Demonstration experiments simulating two applications were performed with satisfactory results.

Application of Holography to Environmental Studies

B. P. Hildebrand

Holography, invented in 1948, is a photographic technique capable of recording a scene in three dimensions. This record, the hologram, can be used to reconstruct the scene for later study. The reconstruction is so perfect that it can be used to make precise measurements by means of interferometry, for example. The invention of the laser in the 1960's resulted in a rapid expansion in research of holography and the search for applications. The pulsed laser, in particular, imparted a momentum in the direction of particle holography since transient events could be recorded and studied in the laboratory.

A Korad 1500 giant pulse laser is being used to determine the resolving capability and optimum optical arrangements for aerosol investigations. The wavelength of the

radiation is 0.6934μ , resulting in a theoretical resolving capability of about 0.69μ . Actual resolution is less than this due to imperfections in the optical components and laser coherence.

A three-bar resolution chart was used to determine the best optical arrangement for aerosol investigations. These studies have shown that the in-line arrangement seen in Figure 3.23 is optimum. The smallest bar spacing in the target is 2μ and we have been able to resolve these. The hologram image is displayed as shown in Figure 3.24. The image may be examined with a microscope, or cast onto a television camera target for display on a monitor. The latter system offers both optical and electronic magnification of the image for ease of observation and measurement.

Observations

The initial experiments described in the introduction were performed without

FIGURE 3.23. Holographic Camera Recording Aerosol Cloud

FIGURE 3.24. Display System for Examining the Holographic Image

Q-switching. This mode of laser operation results in pulses about 0.5 msec in length; too long to resolve moving aerosols. Subsequently, a Q-switch was installed yielding pulse lengths of about 30 nsec, adequate for resolving fast moving particulates.

The experiments mentioned in the abstract were designed to demonstrate two possible applications. In the first experiment we borrowed a nebulizer of the type used in inhalation toxicology studies in Battelle's Biology Department. This device is designed to produce water particles, 5 μ m in diameter. The cloud of water particles was holographed and the image displayed on the television screen. The particles were easily resolved as shown in Figure 3.25. Figure 3.25a shows several particles, only one of which is in focus. The camera can be moved to bring other particles into focus as shown in Figure 3.25b and 3.25c.

The second experiment was performed as a demonstration of the application to under-

water holography. A small aquarium was filled with water containing diatoms. The light beam had to traverse 8 in. of water so care had to be taken to adjust the density of diatoms so that little light would be scattered. This is necessary for good holographic imaging. Figure 3.26 shows two planes of the image within the volume. Figure 3.26a shows an agglomeration of diatoms with two attached air bubbles, one of which is in focus. Figure 3.26b shows another bubble and a diatom of about 10 μ m diameter.

Conclusions

The application experiments have proven that pulsed holography could make a contribution to the study of aerosols and minute aquatic life. However, a simple portable camera must be developed in order for these applications to come to fruition. The next phase of this program will be directed towards this goal.

FIGURE 3.25. Image of Water Droplets from Nebulizer. Arrows point to in-focus drops as the microscope is scanned through the volume. The rings on the left are artifacts of the microscope used to magnify the image.

FIGURE 3.26. Image of Organic Matter (diatoms) and Air Bubbles. Arrows point to in-focus bubbles, double arrows point to organic matter.

• REAL-TIME MEASUREMENT OF Pu IN AIR AT BELOW MPC LEVELS

A direct-inlet mass spectrometer is being developed for monitoring low-level airborne plutonium on a real-time basis. The instrument will be capable of measuring plutonium concentrations below the MPC level. Construction of the spectrometer has been completed. A minicomputer-based data acquisition system is nearing completion. Instrument calibration for absolute particle-size measurement is in progress.

Direct-Inlet Mass Spectrometer Development J. J. Stoffels and C. R. Lagergren

Current techniques for monitoring airborne plutonium are limited by the rate of radioactive decay which, for ^{239}Pu , amounts to only one disintegration per second for every 10^{12} atoms present. A new technique using direct-inlet mass spectrometry is being developed which will measure one ion count for approximately every 10^2 atoms of ^{239}Pu present and do this on an individual particle basis.

A direct-inlet mass spectrometer has been constructed which combines a highly efficient inlet with a very wide dynamic range ion detector in an instrument which can be transported to different locations. Further development of the ion detector has improved noise immunity and speed of response. A minicomputer-based data acquisition and readout system is being developed to handle the large amounts of data which can be generated by the mass spectrometer. Steps are being taken to eliminate mass spectral interferences due to hydrocarbon contamination in the vacuum system. Calibration of the instrument to provide absolute measurements of particle sizes has begun.

The direct-inlet mass spectrometer (DIMS) is a desk-sized instrument (see Figure 3.27) mounted on casters which requires only electrical power for its operation. The instrument includes an additional rack of elec-

tronics which is not shown. The direct air-sampling inlet and the wide-range ion detector were described in the 1975 Annual Report (BNWL-2000, PT4).

Problems of noise and slow response were experienced with the dc channel of the ion detector. These problems were associated with the need to operate the current-measuring electrometer with a 10^{10} ohm input resistor. Improvements have been made to the detector which eliminate these problems. As shown in Figure 3.28, the DC current is no longer taken directly from the aluminum coating on the plastic scintillator. Instead, a fraction of the light produced in the scintillator is piped to a side photomultiplier which is operated at a low gain of about 10^3 . With this gain increase the input resistance of the electrometer can be decreased to 10^7 ohm, effectively eliminating noise pickup and also speeding up response.

A data acquisition and readout system using a PDP-11 minicomputer is nearing completion. The system will integrate the ion-pulse counts and/or the dc current from an ion-burst event, measure the time duration of the event, and readout the resultant data. The minicomputer-based system will be a much more versatile replacement for the hardwired device currently performing these tasks. It will be able to transform the raw data into more meaningful forms, for example, by calculating and plotting particle size distributions.

FIGURE 3.27. Direct-Inlet Mass Spectrometer

FIGURE 3.28. Ion Detector with Simultaneous Pulse Counting and DC Current Modes of Operation for Wide Dynamic Range Response

Mass spectral interferences due to hydrocarbon contamination in the vacuum system have been observed on the DIMS. The interfering spectra extend through mass 280 and are largely due to severe backstreaming of oil from the second-stage pump on the direct inlet. The spectrometer has been completely disassembled, cleaned, and reassembled with traps between both the first- and second-stage pumps and the inlet. Cartridge heaters

have also been installed on the source housing to permit baking of the ion source. How effectively these measures eliminate the spectral background remains to be seen.

Some initial particle size distributions have been measured with the DIMS but the sizes are not absolute. Calibration of the instrument to provide absolute measurements of particle sizes is a major part of the work currently in progress.

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Braby, L. A. - 11, 13, 28
Brodzinski, R. L. - 60
Bushaw, B. A. - 88
Campbell, J. A. - 3
Chaturvedi, R. P. - 39
Crececius, E. A. - 62, 63
Criswell, T. L. - 37
Cross, F. T. - 83
Endres, G. W. R. - 83
Fruchter, J. S. - 67, 71, 74, 76, 79
Hildebrand, B. P. - 92
Kay, J. H. - 85
Kutt, J. C. - 6
Lagergren, C. C. - 95
Laul, J. C. - 3, 55, 59, 67, 74, 76
Ludwick, J. D. - 79
Lynch, D. J. - 39
Manson, S. T. - 30
MacMurdo, K. W. - 55
Miller, J. H. - 43, 45
Nelson, J. M. - 13
Nielson, K. K. - 59, 63, 64
Peterson, M. R. - 67, 71
Popowich, R. J. - 34
Rancitelli, L. A. - 74
Rieck, H. G., - 55
Robertson, D. E. - 79
Roesch, W. C. - 11, 13, 14, 15, 20, 23, 28
Ryan, P. W. - 66
Smith, R. D. - 3
Stoffels, J. J. - 95
Toburen, L. H. - 30, 33, 34, 37, 39
Weimer, W. C. - 6
West, M. L. - 43, 45
Whitaker, T. J. - 88
Wilkerson, C. L. - 62, 72
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