CC: J.H. Craddock
T.G. Nassif
J.D. Wilson
F.D. Hileman



The University of Dayton

3 October 1984

Monsanto Company
ATTN: Mr. Paul Michael
Building N, Lab 122
Research Center
800 North Lindberg
St. Louis, Missouri 63167

SUBJECT: Proposal No. R-5292 for Thermal Decomposition and Product Analysis of Selected Chlorinated Compounds and Dielectric Fluids

REFERENCE: Discussions between Mr. Paul Michael and Dr. Barry Dellinger on 13 September 1984, same subject

Dear Mr. Michael:

The University of Dayton is pleased to submit this proposal as per the referenced discussion. Attached to this letter are the Statement of Work (Attachment 1), Qualifications (Attachment 2), and Cost Estimates (Attachment 3). The cost information is detailed for the Basic Program (Tasks 1, 2, and 3) and Optional Tasks A, B, and C. The tasks that are part of the Basic Program are relatively well defined; however, the optional tasks are contingent upon the findings of the Basic Program and, therefore, are considered preliminary.

With a contract start date of 1 November 1984, the Basic Program (Tasks 1, 2, and 3) would be completed by 30 November 1985. Completion of the optional tasks will depend upon their complexity and date of initiation.

If this proposal is acceptable, a purchase order should be issued to the University of Dayton and sent to the undersigned.

MONS 213827

RESEARCH INSTITUTE
Office of the Director
300 College Park Dayton, Ohio 45469-0001

Should any additional information be required, please contact the undersigned at (513) 229-2919.

Sincerely,

Mrs. Audrey G. Sachs
Assistant to the Contracts
and Grants Administrator

AGS:bay
Attachments

APPROVED BY:

GEORGE B. NOLAND, Ph.D.
Associate Provost/Authorized
Representative

MONS 213828

ATTACHMENT 1

THERMAL DECOMPOSITION AND PRODUCT ANALYSIS OF SELECTED CHLORINATED COMPOUNDS AND DIELECTRIC FLUIDS

STATEMENT OF WORK

The proposed research program has been divided into the Basic Program (Tasks 1, 2, and 3) and Optional Tasks A, B, and C. Task 1 of the Basic Program is a thorough study of the thermal decomposition properties and reaction products of 1,2,4-Trichlorobenzene under various reaction conditions. Task 2 of the Basic Program is a thermal decomposition study of Aroclor 1242 and Aroclor 1254 under reaction conditions defined in Task 1. Task 3 of the Basic Program is the thermal decomposition study of an Ascarel transformer fluid under the conditions defined by Tasks 1 and 2. Optional Tasks A, B, and C are designed to allow additional experiments to address questions raised during the Basic Program.

All work will be performed in the Environmental Sciences Laboratory of the University of Dayton using the Thermal Decomposition analytical System (TDAS) or Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) System. Selected samples will also be collected for analysis by Monsanto.

A. TASK 1 OF THE BASIC PROGRAM - Thermal Decomposition of 1,2,4-Trichlorobenzene

1. During this task, the University will generate the thermal decomposition profile (weight percent remaining versus temperature with a minimum of 6 data points) for a gas phase residence time (t_r) of 2.0 seconds. Profiles will be generated in three reaction atmospheres: air (oxidative conditions), nitrogen (absolute pyrolytic conditions), and a stoichiometric mixture of oxygen in nitrogen (the equivalence ratio equals one,

i.e., ϕ = (fuel/O_2)actual/(fuel/O_2)required = 1). Organic products of incomplete combustion will be identified by mass spectrometry. Selected products of interest will have their identity confirmed and levels quantified. (See Figure 1 for an example of the type of data to be generated.) Considerable technique development work will be completed under this task that will also be used to conduct the subsequent tasks.

2. The University will also generate thermal decomposition and product appearance profiles at t_r = 0.50 and 5.0 seconds for each of two reaction atmospheres selected based on the results described in Paragraph A.1

3. Isomer specific analysis for 2,3,7,8-Tetrachlorodibenzodioxin (2,3,7,8-TCDD) and 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF) will be conducted for three combinations of temperature and residence time for each of the three reaction atmospheres. Analysis for other chlorinated dibensodioxin and dibenzofuran isomers will be conducted by family (TCDD, TCDF, PCDD, and PCDF). Specific analysis for other compounds will be conducted as suggested by the results of Paragraphs A.1 and A.2. Appropriate standards will be provided by Monsanto.

B. TASK 2 OF THE BASIC PROGRAM - <u>Thermal Decomposition of Aroclor 1242 and 1254</u>

1. Organic destruction profiles (total chromatographic response versus temperature at a minimum of six temperatures) will be generated at a residence time of 2.0 seconds for the three reaction atmospheres specified in Paragraph A.1. Also, profiles at residence times of 0.5 and 5.0 seconds will be generated for the two reaction atmoepheres used in Paragraph A.2.

2. The University will identify and profile (if posaible) 2,3,7,8-TCDD and 2,3,7,8-TCDF and selected PIC families (TCDD, TCDF, PCDD, and PCDF) for two selected reaction atmospheres. Specific analysis for other compounds will be conducted as

PIC = [illegible]

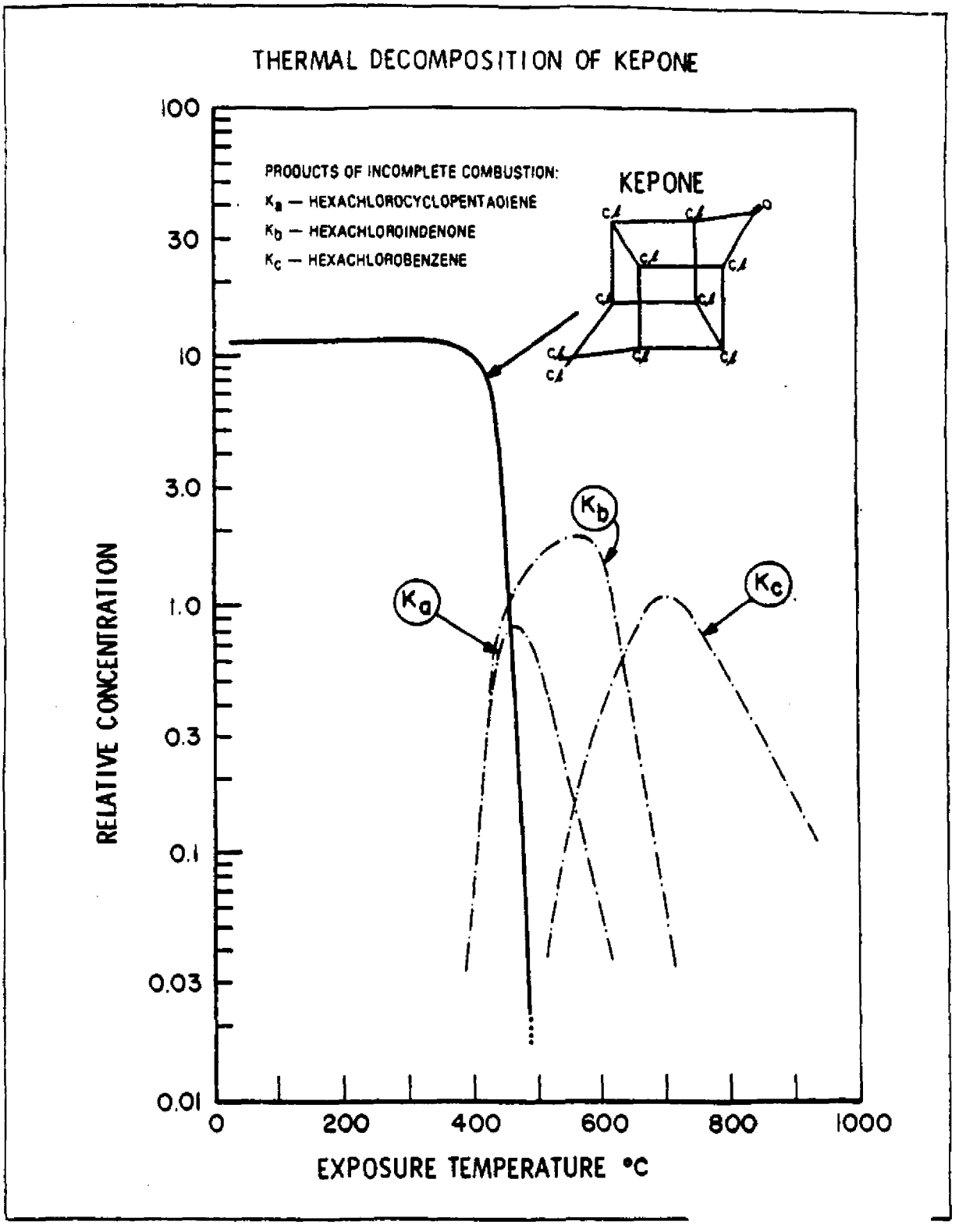

Figure 1.

MONS 213831

suggested by the previous results. Appropriate standards will be provided by Monsanto.

C. TASK 3 OF THE BASIC PROGRAM - Thermal Decompostion of a Selected Ascarel

The Statement of Work for this task is identical to that of Task 2.

D. OPTIONAL TASK A - Thermal Decomposition of Simple Mixtures of 1,2,4-Trichlorobenzene and PCBs

Mixtures of PCBs and 1,2,4-Trichlorobenzene will be studied to explain the possible differences in behavior when the results from Tasks 1 and 2 are compared to the results of Task 3. Changes in thermal stabilities and product identification will be determined (data points at a minimum of 24 reaction conditions).

E. OPTIONAL TASK B - Effects of Radical and Oxygen Scavengers

1,2,4 TCB only

The thermal decomposition properties of the substances tested in Tasks 1, 2, and 3 and Optional Task A will be studied in the presence of radical and oxygen scavengers. Differences in the rates of decomposition and product identities will be determined (data points at a minimum of 24 reaction conditions).

F. OPTIONAL TASK C - Catalytic Effects of Copper Wire

The effects of copper wire, such as the windings in a transformer, will be studied. A catalytic reactor will be constructed and installed. The possible changes in thermal stabilities and product identities will be studied for various Ascarels and other transformer fluid components (data points at a minimum of 24 reaction conditions).

ATTACHMENT 2
QUALIFICATIONS

The University of Dayton is a private coeducational school founded in 1850 with a current enrollment of approximately 10,000 full- and part-time students. The main campus is situated on 75 acres just south of the downtown area of Dayton, Ohio.

Research activities at the University of Dayton are centered in the Research Institute, which was designed to conduct concentrated research programs through the combined efforts of full-time engineers and scientists of many disciplinee, as well as University faculty members. Support is provided by full-time technicians and clerical personnel, with part-time assistance from graduate and undergraduate students. This combination allowe the Institute to provide appropriate technical strengths and staffing flexibility for each research project.

The Director of the Research Institute is also the University's Associate Provost and is responsible for all research activities conducted by the University. The Research Institute conducts studies in eight research areas, each managed by a full-time Project Supervisor. These areas are Materials Engineering (including Environmental Sciences), Aerospace Mechanics, applied Physics, Applied Systems Analysis, Electrical and Computer Engineering, Experimental and Applied Mechanics, Metals and Ceramics, Nonmetallic Materials, and Structural Integrity.

DIRECTLY RELATED EXPERIENCE

Since 1972, the Environmental Sciences Group has been deeply involved in research into thermal decomposition of organic materials and the disposal of hazardous organic substances by incineration. The emphasis of this work has been to determine

their relative thermal stability, the potential for formation of toxic products of incomplete combustion, and identify parameters affecting the thermal degradation process.

Following are brief synopses of some selected research programs conducted by the Environmental Sciences Group. Table I is a partial funding history in the area of hazardous waste incineration.

Thermal Decomposition Instrumentation Development

Thermal instrumentation development has played a major role in the University of Dayton Research Institute's (UDRI) Environmental Sciences Group. The design of the Discontinuous Thermal System (DTS) in 1974 was the first system which could study, in a laboratory setting, the thermal decomposition behavior of organic compounds being considered for disposal by incineration.

Incorporating the basic design principles of the DTS into a closed continuous system resulted in the design of the Thermal Decomposition Analytical System (TDAS). The TDAS features an in-line capillary column gas chromatograph and couples mass spectrometer (GC/MS). The use of high-resolution GC-MS techniques endow the TDAS with tremendous versatility and analytical capabilities. In addition, the TDAS can readily detect and identify stable PICs and handle large quantities of information with the aid of a dedicated minicomputer.

The need for a lower cost system which could rapidly analyze trace amounts of PICs and still conduct parent compound decomposition studies prompted the development of the Thermal Decomposition Unit-Gas Chromatograph. In the TDU-GC, the GC/MS has been replaced by a versatile high-resolution gas chromatograph with a dedicated microprocessor and options for the large assortment of trace analysis detectors.

MONS 213834

TABLE I

PARTIAL FUNDING HISTORY OF HAZARDOUS WASTE DISPOSAL RESEARCH

PROJECT TITLE	SPONSOR	DATE	AMOUNT FUNDED
Investigation of Gas-Phase Thermal Decomposition Properties of Hazardous Organic Compounds	EPA	1983-86	$1,022,371
Design, Fabricate, and Supply a System for Thermal decomposition Studies	Canadian	1984	79,995
Generation of Gas-Phase Thermal Decomposition Profiles	Canadian EPS	1983-84	14,993
Development of Thermal Destruction Profiles for Hazardous Wastes Using Thermal Decomposition Analytical System	EPA	1980-83	373,462
Use of Advanced Thermal Systems for Studying Decomposition of Hazardous Organic Waste	EPA	1980-83	362,056
High-Temperature Degradation Characteristics of Hazardous Organic Wastes--A Laboratory Approach	EPA	1977-80	355,313
Laboratory Evaluation of the Thermal Decomposition of Pesticides	EPA	1975-77	117,451

MONS 213835

An instrument called the Packaged Thermal Reactor System (PTRS) was developed to provide a portable, low cost, simple to operate device which can produce basic thermal decomposition data quickly and in a variety of environments. A desk top sized prototype unit has been completed and a more advanced field-ready system is under development.

Also under development is the System for Decomposition Studies (STDS). The STDS incorporates the developments and advantages of the previous systems with the added flexibility of conveniently interchangeable reaction test cells and analytical inatrumentation. With this system, it will be possible to investigate an expanded list of incineration variables and parameters.

Pesticides

The thermal decomposition characteristics of numerous pesticides have been investigated in our laboratory. Among these is the controversial pesticide, DDT. Although researchers at UDRI found this pesticide to be thermally labile, it was observed that rather than being degraded to thermodynamic end products, DDT was converted to a thermally stable compound, DDE. In full-scale test burns of DDT, DDE has in fact been found to be the major PIC.

In 1976, the Environmental Sciences Group submitted a report culminating three months of intensive research effort to determine the high-temperature destruction characteristics of the pesticide Kepone. UDRI researchers generated thermal destruction versus temperature profiles of the pesticide at various hot-zone residence times. It was clear from these profiles that the incineration of Kepone would be strongly dependent upon both the temperature and the residence time in the incinerator. More important, under certain conditions, Kepone did not simply decompose into harmless products, but instead formed hazardous products

of incomplete combustion. Our report was presented to the special EPA Kepone Task Force, which was investigating solutions to the Kepone contamination in and around Hopewell, Virginia, and in the James River. Information contained within this report confirmed high-temperature incineration as a safe means of Kepone disposal and provided guidance for a successful followup pilot-scale burn. This research effort was cited by the US-EPA as an outstanding example of a most successful university grant from every perspective--results, cooperation, professionalism, and mutual respect.

Industrial Wastes

Improper disposal of industrial wastes in another route of environmental contamination by toxic chemicals. In 1977, the Environmental Sciences Group was asked by the US-EPA to assess incineration as a possible method of detoxifying an industrial waste sludge which had been illegally dumped in the Louisville, Kentucky sanitary sewage system. Although UDRI researchers revealed over 185 distinct chemical compounds in the waste mixture, conditions were established for destruction of the waste and the products resulting from the incineration process. Once again, a difficult environmental problem was solved and guidelines were developed for eliminating a potential health hazard.

PCBs

As a result of early successes in establishing the operating parameters for safe incineration of toxic chemicals, the Environmental Sciences Group expanded its efforts to include numerous other industrial mixtures and pure compounds. Many instances in which effluent products are more hazardous than the feedstock have since been observed, as in the case with the formation of chlorinated dibenzofurans from polychlorinated biphenyls (PCBs). The considerations favoring such reactions are readily identified in the laboratory. These adverse conditions

can then be avoided in the field, ensuring environmentally safe incineration.

Pure Organic Compounds

Kinetic parameters derived from the thermal decomposition of pure compounds are being used to develop a ranking of "incinerability" by the US-EPA. This is currently the only such comprehensive study underway. It will provide a valuable guide for incineration permit application reviewers. These data are also being used by scientists and engineers who are developing or applying comprehensive incineration models.

In addition, selected compounds are being studied to determine the pathways of thermal decomposition and formation of products of incomplete combustion. The effects of composition of the reaction atmosphere on these pathways is currently an area of continuing investigation.

FACILITIES AND EQUIPMENT

The activities of the Environmental Sciences Group are performed in seven different laboratories which are located within the Eugene W. Kettering Engineering and Research Laboratories. This building was constructed in 1969 on the University of Dayton campus, and an annex built in 1978 added laboratory and office space in this facility to approximately 56,000 square feet. In addition, the Research Institute occupies slightly more than 58,000 square feet in other buildings of the University.

Environmental Sciences Laboratory

The seven laboratories of the Environmental Sciences Group are located in one interconnected complex and constitute approximately 2,100 square feet of floor space (see Figure 2). Three of these laboratories are dedicated to conducting thermal decomposition studies with special analytical instrumentation that has

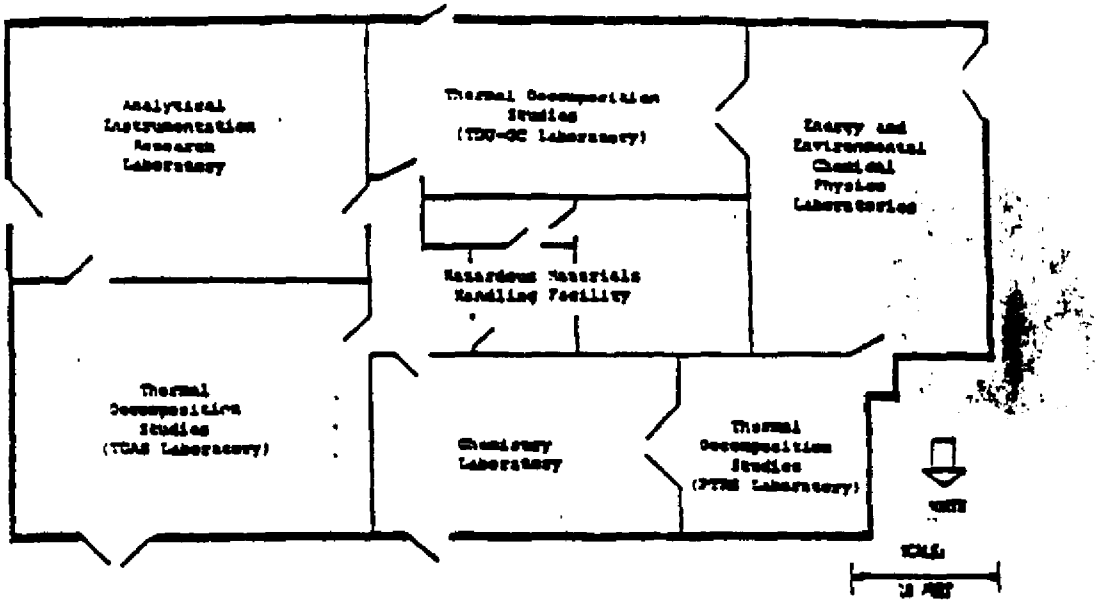

Figure 2. Environmental Sciences Laboratory.

been designed and developed at the University of Dayton. The Energy and Environmental Chemical Physics Laboratory is equipped with advanced lasers and optical systems to study elementary chemical and physical processes associated with gas-phase reactions of environmentally sensitive materials. In addition, there is a laboratory that is devoted to analytical instrumentation research in the fields of high-resolution gas chromatography and thermal instrumentation system development. The hub of this laboratory complex is a hazardous material handling facility, which is fully equipped for dealing with toxic organic substances as it has a minimum of five levels of containment. This hazardous materials handling facility, along with a general chemistry laboratory, enhances our capabilities to prepare and analyze highly toxic organic substances. A listing of major equipment housed in these laboratories is presented in Table II.

Support Facilities

The support facilities of the Research Institute contain a full range of standard research equipment and apparatus appropriate to the Institute's programs. Much of this apparatus has been extensively modified and adapted to perform beyond its original design capability. In addition to the standard equipment, the laboratories contain many items of highly specialized equipment for support of advanced research programs. The laboratories and shops provide capabilities that are not easily obtainable from outside sources; in some cases the services they provide are not available anywhere on a commercial or contractual basis outside the University of Dayton.

RESUMES

The following pages contain resumes of the Principal Investigator and key staff assigned to this program.

TABLE II

MAJOR EQUIPMENT CONTAINED IN THE
ENVIRONMENTAL SCIENCES LABORATORIES

Thermal Decomposition Equipment

Thermal Decomposition Analytical System
Thermal Decomposition Unit Gas Chromatograph
Packaged Thermal Reactor System

Laser Systems

Quanta Ray DCR-2 Nd:YAG Laser
Quanta Ray PDL-1 Dye Laser
Quanta Ray EXC-401 EXCIMER Laser

Analytical Equipment

LBK Model 2091 GC-Mass Spectrometer
Varian Model 1800 Gas Chromatograph
Varian Model 2400 Gas Chromatograph
Varian Model 3700 Gas Chromatograph (Modified)
Varian Model Vista 44 Gas Chromatograph (Modified)
Tracor Model 550 Gas Chromatograph (Modified)
Beckman DK-2A Recording Spectrophotometer

Computer Support

Digital VAX 11/780 (Accessible)
UNIVAC 90/80-3 (Accessible)
Digital PDP 11/04
Apple IIe and Epson Printer

MONS 213841

BARRY DELLINGER — Principal Investigator, Group Leader

Education

B.S. degree, Chemistry, University of North Carolina, 1971
Ph.D. degree, Physical Chemistry, Florida State University, 1975

Experience

Dr. Dellinger is Group Leader of Environmental Sciences at the University of Dayton Research Institute, where he is directly involved in research as well as responsible for technical direction and management of a team of professional scientists and engineers. His group is currently involved in research into the thermal decomposition properties of organic materials and incineration of hazardous wastes. This work involves the development of laboratory data and theoretical models that can be used to determine the thermal stability of various organic materials as well as predict the products of incomplete combustion resulting from thermal exposure. He is currently Principal Investigator on EPA Coopertive Agreement CR-81078.

Dr. Dellinger has been directly involved and has experience in a diversity of research areas. Trained as a physical chemist, he has a strong background in spectroscopic techniques, kinetics, thermodynamics, and aerosol physics. As a postdoctoral research fellow at the University of Pennsylvania, he conducted an interdisciplinary program on the laser-induced decomposition of organic molecules. This expertise has been most recently applied to establish the Energy and Environmental Chemical Physics Laboratory within the Research Institute. This laboratory will primarily be used to study the elementary reactions key to combustion, incineration, and atmospheric chemistry.

Selected Publications

B. Dellinger, J. L. Torres, W. A. Rubey, D. L. Hall, J. L. Graham, and R. A. Carnes, "Determination of the Thermal Stability of Selected Hazardous Organic Compounds," Hazardous Waste, Vol. 1, No. 2, p. 137, 1984.

MONS 213842

B. Dellinger, J. L. Torres, W. A. Rubey, D. L. Hall, J. L. Graham, and R. A. Carnes, "Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds," Presented at the Tenth Annual SHWRD Research Symposium in Ft. Mitchell, Kentucky, April 1984.

B. Dellinger, D. L. Hall, W. A. Rubey, J. L. Torres, and R. A. Carnes, "Factors Affecting the Thermal Decomposition of Chlorinated Hydrocarbons," Presented at the Ninth Annual SHWRD Research Symposium, Cincinnati, Ohio, May 1983.

B. Dellinger, J. L. Torres, and R. A. Carnes, "The High-Temperature Gas-Phase Oxidation of Selected Chlorinated Aliphatic and Aromatic Hydrocarbons," Presented before the Division of Environmental Chemistry of the American Chemical Society, Seattle, Washington, April 1983.

B. Dellinger, D. S. Duvall, D. L. Hall, W. A. Rubey, and R. A. Carnes, "Labotory Determination of High-Temperature Decomposition Behavior of Industrial Organic Materials," Proceedings of 75th Annual Meeting of Air Pollution Control Association held in New Orleans, June 1982.

C. R. Fortune and Barry Dellinger, "Stabilization and Analysis of Sulfite in Environmental Samples," Env. Sci. and Tech., Vol. [illegible] 1982.

J. Lorrain, C. R. Fortune, and B. Dellinger, "Sampling and Ion Chromatographic Determination of Formaldehyde and Acetaldehyde," Anal. Chem., Vol. 53, p. 1302, 1981.

B. Dellinger, G. Grotecloss, C. R. Fortune, J. L. Cheney, and J. B. Homolya, "Sulfur Dioxide Oxidation and Plume Formation at Cement Kilns," Env. Sci. and Tech., Vol. 14, p. 1244, 1980.

B. Dellinger, M. A. Paczkowski, R. M. Hochstrasser, and A. B. Smith, III, "Observation of Transient Intermediate in the Photochemical Decomposition of Substituted s-Tetrazines," J. Am. Chem. Soc., Vol. 100, p. 3242, 1978.

B. Dellinger, D. S. King, R. M. Hochstrasser, and Amos B. Smith, III, "Laser Induced Isotope Enrichment in a Rare Gas Matrix," J. Am. Chem. Soc., Vol. 99, 1977.

B. Dellinger and M. Kasha, "Phenomenology of Solvent Matrix Spectroscopic Effects," Chem. Phys. Letters, Vol. 38, 1975.

B. Dellinger and M. Kasha, "Intermolecular Pertubation of Molecular Potentials," Chem. Phys. Letters, Vol. 36, 1975.

MONS 213843

DOUGLAS L. HALL — Associate Environmental Chemist

Education: — B.S. degree, Chemistry, Wright State University, 1977

Experience:

Mr. Hall is presently an Associate Environmental Chemist in the Environmental Sciences Group at the University of Dayton Research Institute. His laboratory duties include the operation and maintenance of the Thermal Decomposition Analytical System and associated LKB 2091 GC-MS. His responsibilities include supervision of technicians and students, maintenance of instrumentation systems, maintenance of chemical and supplies inventory, and acquisition and interpretation of laboratory data.

His current research concerns the effect of oxygen concentration on the thermal stability of hazardous organics. He is also involved in the determination of pathways for the formation of products of incomplete combustion resulting from the high-temperature thermal degradation of hazardous organic materials.

He is knowledgable and experienced in the use of numerous instrumentation systems. In addition to the GC-MS systems which he presently operates, these techniques include quadrupole mass spectrometry, and atomic absorption spectrometry.

He has extensive experience in the area of surface chemistry and has used mass spectrometry in conjunction with volumetric thermal desorption in his studies. He has participated in the design of computer software for automation of experimental control and data acquisition and has modified software to expand their utility.

Mr. Hall, in addition to fulfilling his duties in the Environmental Sciences Group, is working toward an M.S. degree in Chemistry from the University of Dayton.

MONS 213844

WAYNE A. RUBEY

Environmental Scientist

Education:

A.T. degree, Mechanical Engineering Technology, Sinclair College, 1956
B.T. degree, Mechanical Engineering Technology, University of Dayton, 1968

Experience:

Mr. Rubey is presently an Environmental Scientist in the Environmental Sciences Group at the University of Dayton Research Institute. He is responsible for the design and development of thermal analysis instrumentation and technical direction of various research programs concerning the thermal degradation analysis of hazardous organic compounds. He is currently Co-Principal Investigator for EPA Cooperative Agreement CR-810783, Investigation of Gas Phase Thermal Decomposition Properties of Hazardous Organic Compounds.

Mr. Rubey has for the past several years been designing thermal analysis systems for studying the thermal decomposition properties of pesticides and various hazardous organic materials. His initial thermal decomposition system, which was designed in 1976, was of vital importance in establishing the thermal decomposition properties of toxic substances such as Kapone, Mirex, DDT, and PCB's. More recently he has designed two highly sophisticated systems known as a thermal decomposition analytical system (TDAS) and the thermal decomposition unit-gas chromatograph (TDU-GC). These systems have been major tools for evaluating the permanent disposal potentials via incineration of a wide variety of toxic organic substances. Mr. Rubey is presently involved in the design and development of additional thermal instrumentation systems, namely a packaged thermal reactor system and a system for thermal decomposition studies (STDS). Each system is being or has been designed to generate environmentally important fundamental thermal decomposition data in a rapid, economical, and safe manner.

MONS 213845

Mr. Rubey has also applied basic fluid mechanic principles in the specialized area of high-resolution GC column technology. He has devoted considerable attention to the study of the fundamental dispersion processes which occur in open flowpath gas chromatographic columns. He has designed and fabricated a wide variety of high-performance GC separation columns.

In addition, he is involved with developing high-rasolution gas chromatographic analytical methods. Mr. Rubey is conducting studies for the U.S. Air Force, where the objective is to obtain optimized high-resolution GC techniques for analyzing shale oil products and various petroleum-based jet fuels.

Prior to joining the University of Deyton Research Institute, Mr. Rubey acquired eight years of laboratory experience involving electromechanical development and instrument calibration projects.



ATTACHMENT 3

COST INFORMATION

The cost for this effort is outlined below. This effort has been costed on a best efforts, cost-reimbursement basis.

BASIC PROGRAM		$120,996
Task 1	$47,985 ~~6 months~~	
Task 2	37,778	
Task 3	35,233	
OPTIONAL TASK A		$ 28,958
OPTIONAL TASK B		$ 28,958 ~~just TCB~~
OPTIONAL TASK C		$ ~~38,961~~ just TCB 49,961

These costs are valid for a period of 60 days.

~~HH9H~~

MONS 213847