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CHARACTERIZATION OF COAL-DERIVED LIQUIDS AND OTHER FOSSIL FUEL RELATED MATERIALS EMPLOYING MASS SPECTROMETRY

Quarterly Report for the Period
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Stuart E. Scheppele

The Oklahoma State University
Department of Chemistry
Stillwater, Oklahoma 74074

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CHARACTERIZATION OF COAL-DERIVED LIQUIDS AND OTHER FOSSIL FUEL RELATED MATERIALS EMPLOYING MASS SPECTROMETRY
(FE 2537-1)

ABSTRACT

A two-part report is being prepared which assesses both the current state-of-the-art in mass spectral analysis of alternate fossil fuels and the needs of technical personnel for characterization data. To acquire the requisite information for preparation of this document, discussions were held with appropriate individuals at the Pittsburgh, Morgantown, and Bartlesville Energy Research Centers, Gulf Research, and Exxon Research and Engineering Company.

An evaluation of commercially available data acquisition systems suitable for use with our CEC 21-110B double focusing mass spectrometer was made. This study resulted in both the selection and development of specifications for the components for the basic data system; provision has been made for future hardware and software expansion. The status of our comparator/microdensitometer was determined and procedures were initiated to make it mechanically functional.

Study of the dependence of field ionization sensitivities for mixtures of saturates and aromatics was conducted, in part, under this contract. Modification of our FI/EI ion source to operate in the FD mode and construction of ancillary equipment was supported, in part, by this contract. Programs for processing micromolecular probe distillation data have been made operational on the OSU IBM 370/158. Collaborative characterization research with J. E. Dooley's Group at BERC and with B. L. Crynes' Group at OSU was supported, in part, by this contract.

OBJECTIVE AND SCOPE OF WORK

The objectives of this program are as follows. First, to develop new and refine existing mass spectrometric techniques for obtaining routine and detailed characterization data for coal-derived liquids and other fossil fuel related materials. The existing mass spectrometer facilities are being augmented by addition of a dedicated data acquisition system, a comparator/microdensitometer, a temperature control display module for the solid introduction probe inlet, modification of the FI/EI source to operate in the field desorption mode, and ancillary gas chromatographic equipment. Hardware and software to permit computer acquisition and processing of data from the mass spectrometer and peripheral instrumentation will be developed in detail. Using this augmented system, the following techniques will be routinely applied to the characterization of fossil fuels: a) high- and low-resolution electron-impact, field-ionization, and field-desorption mass spectrometry and b) micromolecular probe distillation and simulated distillation in conjunction with mass analysis. The utility of the newer techniques for conducting such analyses will also be evaluated. Second, the existing mass spectrometer facility and the equipment being acquired and the associated analytical methodologies available and under development will be used to obtain analytical data for other ERDA sponsored projects. Third, preparation of a document for ERDA which assesses both the current state-of-the-art in mass spectral analysis of alternate fossil fuels and the needs of technical personnel for characterization data. Fourth, to provide interdisciplinarily trained analysts capable of meaningful participation in the overall effort to achieve greater national energy independence and in other contemporary scientific problems of national significance.

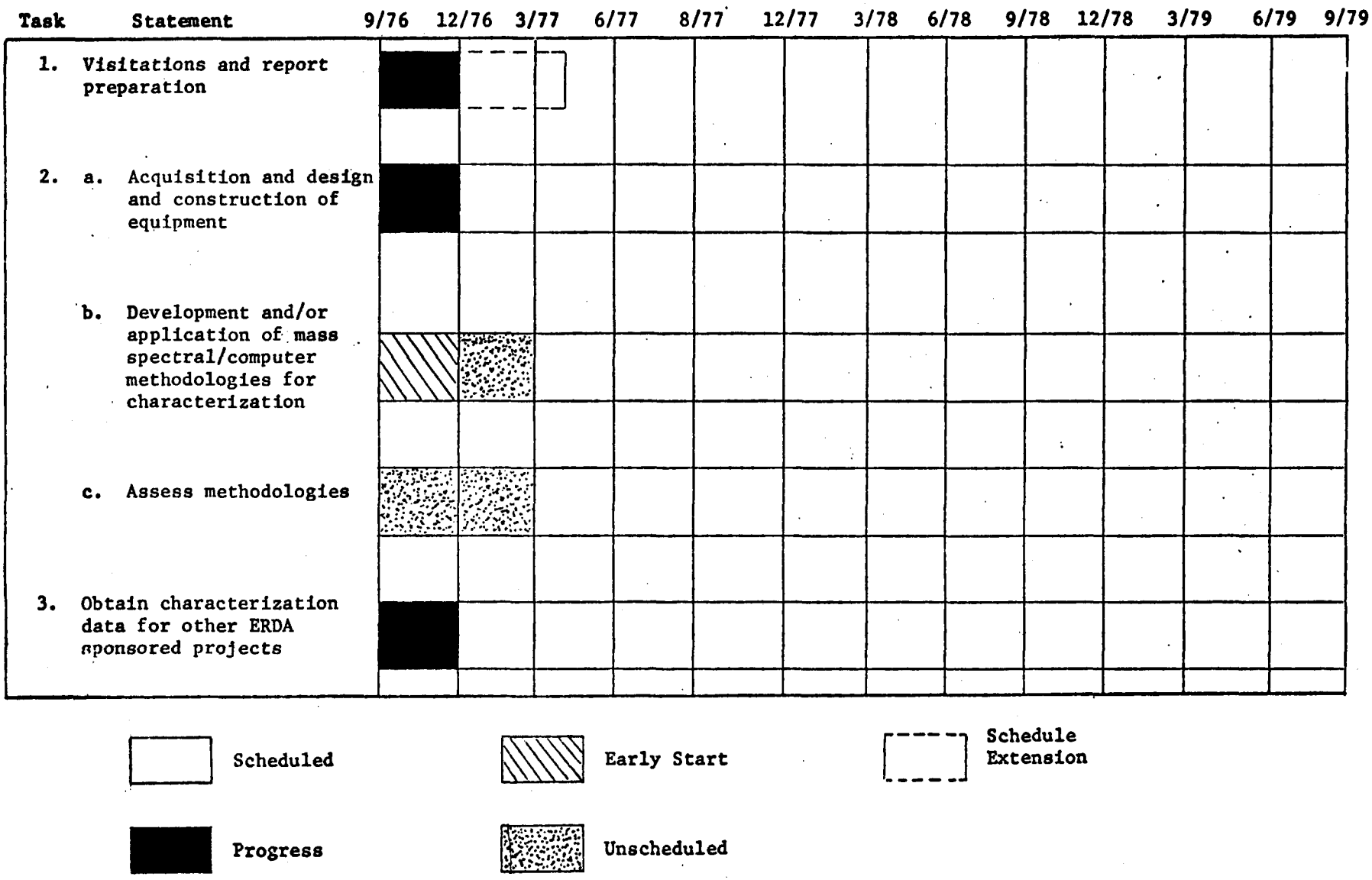
SUMMARY OF PROGRESS TO DATE

The following chart summarizes the progress to date. The scheduled time for completing the report concerning mass spectral characterization of alternate fossil fuels and the technical need for such data (Task 1) had to be extended because of time requirements and the imperative need to commence a number of Task 2 activities. Discussions were held with appropriate individuals at approximately 36% of the laboratories to be visited. Task 2 activities include: 1) selection and development of specifications for the basic data acquisition system to be purchased, 2) evaluation of the status of our comparator/microdensitometer and initiation of procedures to make it mechanically operational, 3) implementation of computer programs for processing micromolecular probe/mass analysis data on OSU IBM 370/158, and 4) support of both field ionization sensitivity research and development of our field-desorption capability. Support of our characterization research in collaboration with J. E. Dooley's and B. L. Crynes' ERDA-sponsored projects at BERC and OSU, respectively, constitute Task 3 activities.

As of December 29, 1976, 3.5% of the total budget has been spent. This rate of expenditure is consistent with our schedule.

PROGRESS SUMMARY AS OF DECEMBER 29, 1976

Schedule as of the 29th day of month/year



DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 — Preparation of a Document Which Assesses Both the Current State-of-the-Art in Mass Spectral Analysis of Alternate Fossil Fuels and the Needs of Technical Personnel for Characterization Data

To acquire sufficient data for preparation of this document, various laboratories currently performing mass spectral characterization of fossil fuels are being visited. The Pittsburgh, Morgantown, and Bartlesville Energy Research Centers, Gulf Research, and the Exxon Research and Engineering Company have been visited to date.

The approach adopted in document preparation is to draft a summary of the discussions held with the various individuals at each laboratory and then return the summary for their comments. The individual summaries will then be suitably combined into a two-part report. The first part, suitable for general distribution, will summarize the needs for and the areas of applicability of mass spectral characterization in the development of fossil-energy reserves. In applying mass spectrometry to the characterization of fossil fuels, Part Two will, in detail, a) assess the present status of the applicable technology, b) comment on needed technological developments, and c) discuss the ultimate limitations of the technique. In addition, coordination and development of supportive programs will be discussed.

This two-part report was originally scheduled for presentation as part of this first quarterly progress report. However, this schedule was found to be incompatible with 1) the time required for the various visits and the need for additional communication with the individuals visited (this will be achieved by the use of the previously mentioned summaries) and 2) the imperative need to commence a number of Task 2 activities, especially the development of specifications required for the data acquisition system. Consequently, the situation was reviewed with the Technical Project Officer, Dr. Paul C. Scott, Program Manager, Fossil Energy Research at ERDA and an extension on Task 1 completion time was approved.

Detailed summaries have either been or are being prepared from notes taken of meetings held at PERC, MERC, BERC, and Gulf Research. The PERC summary comprises ca. 25 double-spaced typewritten pages. Discussions held at Exxon Research and Engineering with Thomas Aczel and Earl Lumpkin were recorded and with process engineers were summarized on tape. The transcription of these tapes comprises ca. 36 double-spaced typewritten pages and is currently being edited. The taping of relevent portions of discussions has proven useful and will be continued.

Interviews conducted to date demonstrate that separations constitute a necessary adjunct to the characterization of alternate fossil fuels. Consequently, the contribution of chemical/physical separation to fossil-fuel characterization and the available separation methods will be presented. Since other instrumental techniques compliment mass spectral characterization, the applicability of techniques such as ^{1}H and ^{13}C nuclear magnetic resonance, electron spin resonance, and infrared spectroscopy will be considered. In order to be consistent with the stated format of and to limit the size of the report, no attempt will be made to 1) evaluate the various separation techniques, and 2) supply technical details for application of neither the various separation methodologies nor the other instrumental techniques.

Broad categories involved in the characterization of alternate fossil fuels which are emerging from these discussions include:

1) the applicability and limitations of present mass spectrometric instrumentation in sample analysis.
2) the need for developing new or adapting certain existing mass spectral methodologies for analyzing various compound classes.
3) consideration of the need for a new generation of multi-purpose mass spectrometers.
4) the status of techniques for converting ion abundances into quantitative distributions and the need for additional research in this area.
5) the effective use of computer technology in acquiring, reducing, and interpreting characterization data.
6) the importance of physical/chemical separations to characterization research.
7) the synergistic contributions of other instrumental techniques.
8) the utility of present and the need for additional developments in gas chromatographic technology especially in combination with mass analysis.
9) the significant contributions characterization makes to 1) both fundamental and short-term process and plant development, 2) the quality control of existing on-stream processes, 3) the development and calibration of routine analytical techniques, and 4) the assessment of the environmental, biological and economic consequences of fossil energy conversion.
10) the necessity for interactive communications between analysts and individuals involved in process development.
11) the need for establishment of supporting research programs.
12) the desirability of establishing more effective communication between groups participating in fossil energy characterization and the need for systematic planning in the areas of facility utilization and equipment acquisition.

Work Forecast

Visits to the Laramie and Grand Forks Energy Research Centers are scheduled; a date has been established for a visit to Amoco Oil Company. Arrangements are currently being made to visit the Stanford Research Institute and Chevron Research in California and the Mobil Research facilities in both Paulsboro and Princeton, New Jersey; Dr. P. A. Wadsworth has extended an invitation to visit Shell Development in Houston (see also Task 2). The desirability of visiting the Exxon facility in Linden, New Jersey and the Oak Ridge National Laboratory will be decided. A summary of each visit will be drafted and returned to the appropriate individuals at each laboratory for their comments. The updated summaries will then be suitably combined into the two-part report.

Task 2 — Modification and Augmentation of Existing Mass Spectrometer Facilities and Their Application to the Routine Characterization of Fossil Fuels

Task 2 research is under the direction of S. E. Scheppele and G. E. Hedrick in the Departments of Chemistry and Computer Science, respectively. Other individuals participating in these activities are: T. D. Marriott, G. J. Greenwood, P. A. Benson, and N. B. Perreira. During the first quarter of this contract a detailed evaluation of data acquisition systems for our CEC 21-110B double-focusing mass spectrometer was performed. This evaluation was accomplished in the following steps:

1. Our perceived requirements were listed.
2. Telephone interviews with other users of data acquisition systems were held.
3. Personal interviews were conducted with selected users of data acquisition systems.
4. Telephone conversations were conducted with suppliers of data acquisition systems.
5. Sales representatives and technical personnel from data acquisition companies visited Oklahoma State University.
6. Our perceived list of requirements was updated in terms of the results obtained from items 1 through 5 above.

Detailed analysis of the available high/low resolution data acquisition systems led to the development of a list of criteria for the data acquisition system to be acquired. These criteria were developed from separate hardware and software considerations. The data acquisition systems currently available for double-focusing mass spectrometers were then evaluated in terms of their immediate capability for permitting us to meet our research commitments under this contract. The criteria necessary for successful completion of our research activities include: 1. relatively stable software; 2. the ability to immediately acquire high- and low-resolution mass spectral data; 3. software for the routine reduction of the acquired data and both the hardware and software for its reproduction; 4. standard library search routines; 5. standard routines for acquisition and processing of GC/MS data; 6. the capability for expanding software especially in regard to the acquisition of data from instrumentation peripheral to the mass spectrometer; 7. the ability to add more data gathering capability; 8. a computer manufacturer-supplied operating system; 9. a minimum high speed memory (MOS or core) of 96 K x 16 bits; 10. interface boards with at least one 8-way multiplexor and all required analog-to-digital converters, and digital-to-analog converters; 11. a visual display unit; 12. a printer/plotter; 13. a card reader; 14. an interface to the computer center system IBM 370/158; 15. a console unit such as a DEC writer.

The cost of the various components in the data system was determined. The cost of the complete system exceeds the amount budgeted for the data system. However, a basic system will be acquired which provides the capability for 1) meeting our research commitments under this contract and 2) future expansion in terms of both its hardware and software.

We were the recipient of the comparator/microdensitometer part of a Grant/Datex/CEC system for automatic recovery of mass spectral data recorded on photographic plates from the DuPont Corporation. Detailed inspection of the comparator/microdensitometer revealed that the following items were missing: 1. 120 VDC power supply; 2. 3000 power supply; 3. encoder and X-drive motor;

4. lens system; 5. quartz iodine intensity lamp and the lamp cooling and housing system; 6. interconnecting cables for power supplies and the encoder/X-drive motor. In addition the photomultiplier housing is loose at the chopper motor assembly. Since it was ascertained that the unit could be made operational at a cost considerably less than the cost of a new comparator, arrangements have been made for the installation, alignment, and assembly of the unit in our laboratory. The Hewlett-Packard 6443B 120 VDC power supply has been received and the HP 6110A 3000 VDC power supply and the quartz iodine lamp have been requisitioned. The zoom lens assembly has been acquired by Drs. Turner and Tyler who will complete the mechanical installation of the comparator in our laboratory; in this regard a Fluke 411B 3000 volt VDC has been obtained on a temporary basis.

The applicability of micromolecular probe distillation in conjunction with field ionization mass spectrometry to the characterization of the fraction of a fossil fuel derived material distilling up to ca. 350°C and at ca. 2×10^{-6} torr will be evaluated. Application of the technique involves distillation of a weighed quantity of the sample from the direct solids introduction probe into the mass spectrometer ion source, recording of the field ionization mass spectrum of the volatiles as a function of probe temperature, acquisition of the mass spectral data and the probe temperatures, and computer processing of the acquired data. The applicability of the technique has been demonstrated for both the quantitative and qualitative analysis of relatively simple mixtures using electron impact mass spectral analysis by Professor R. D. Grigsby and his group at Texas A&M University (1). However, the technique of probe distillation in conjunction with FI mass analysis has inherent potential for either the less-detailed analysis of fossil fuel derived materials which have been subjected to little or no prior separation or the more-detailed analysis of fractions obtained from the chemical/physical separation of such materials.

The peak intensity correction and elimination curve fitting computer programs obtained from Professor R. D. Grigsby at Texas A&M University have been implemented on the Oklahoma State University IBM 370/158 computer.

The peak intensity correction program accepts ion intensity data at each m/e value as a function of probe temperature. These data are then corrected for the possible decrease in mass spectrometer sensitivity with increasing ion-source pressure which may occur as a function of the uniform increase in probe temperature. Mass spectrometer sensitivity is monitored by recording intensities of various PFK ions produced from the ionization of perfluorokerosene which is introduced at a constant rate into the mass spectrometer ion source from the all-glass inlet system during the micromolecular distillation. Peak intensities are corrected using Equation 1. In Equation 1, PI(Temp) is the intensity of a given

$$PI(Temp)_{Corrected} = PI(Temp)\left[\frac{PFK(Ave)}{PFK(Temp)}\right] \qquad (1)$$

ion at a specific temperature, PFK(Temp) is the average of the intensities of up to 7 ions in the mass spectrum of perfluorokerosene at that temperature, and PFK(Ave) is the average of up to 7 ions in the mass spectrum PFK averaged over all temperatures. The field-ionization mass spectrum of perfluorokerosene obtained using low-temperature conditioned emitters displays few ions. Consequently, a mixture of compounds will most probably have to be used for monitoring purposes unless field-ionization mass spectra are obtained using high-temperature conditioned wire emitters. At the present time, the corrected peak intensities are punched on

cards for input to the elimination-curve fitting program. However, in future applications with the data acquisition system these ion intensities will be stored on disc rather than punched onto computer cards.

The elimination-curve fitting program fits the corrected experimental intensity data to Equation 2. In Equation 2, I is the calculated intensity at

$$I = \frac{A\exp(-B/T)}{1 + \exp[C(T-D)]} \qquad (2)$$

a given m/e value, T is the temperature in °K, and A, B, C, and D are parameters obtained from mathematically evaluating the variation in the corrected experimental intensities for a given m/e value as a function of probe temperature. The adjusted parameters A and B describe the increasing portion of the elimination curve and the adjusted parameters C and D describe the decreasing portion of the elimination curve. A Simpson's Rule integration is then applied to the calculated intensities to obtain the area under the elimination curve for each ion. This area is proportional to the quantity of a compound having a given molecular weight distilled from the probe within the temperature range of the elimination curve. The areas under the various elimination curves and the appropriate gram or mole sensitivities can be combined to obtain quantitative distributions according to weight or mole percents, respectively.

Use of FI/MS to determine compositional data for saturates requires knowledge of the sensitivity of these compounds towards ionization by high-electric fields. Sensitivities have been reported and metastable spectra investigated for field ionization of a series of saturates (2). The significance of this investigation is not clear since other determinations of FI sensitivities for mixtures of saturates and saturates plus low-molecular weight aromatics indicates that these sensitivities are dependent on mixture composition (3-5). It is important to note that low-ion-source temperatures were used in these latter studies. In this regard, studies in our laboratory (6) show that relative sensitivities for field ionization of aromatic compounds obtained at high-ion source (emitter) temperature are independent of mixture composition. Consequently, a systematic investigation of saturate FI sensitivities as a function of mixture composition, emitter temperature, the average thermal energy of the neutrals, ion-source pressures, and emitter potential has been initiated. The purpose of these investigations is to determine the applicability of FI/MS for the quantitative analysis of 1) saturate mixtures and 2) saturate and aromatic mixtures which would negate the need for separation of such mixtures into saturates and aromatics prior to their analysis. Field ionization sensitivity data will also be obtained for additional saturated hydrocarbons and for single-ring aromatic hydrocarbons substituted with long-chain alkyl groups. In order to expedite this research, we have combined activities under ERDA projects E(34-1)-0020, E(49-18)-2537, and E(49-18)-2011. Preliminary results obtained from our investigations of benzene/heptane mixtures have been summarized (7,8) and will be discussed in detail in a manuscript to be submitted to *Anal. Chem.*. Preliminary results obtained from our investigation of ethylbenzene/decane mixtures have also been recently summarized (9). Consequently, these results will not be discussed in this report.

Our combined FI/EI ion source is being modified to operate in the FD mode. Task completion is being expedited by combining activities under ERDA contracts E(34-1)-0020, E(49-18)-2537 and 4(49-18)-2011. Design and fabrication of the

various components such as the emitter probe, emitter holder, power supplies, activation and etching cells, and vacuum system either have been completed or are in progress. Since this progress has been described in other Quarterly Progress reports (7,8,9) it will not be discussed in this report.

Work Forecast

A requisition listing the components and detailed specifications for our mass spectrometer data acquisition system has been developed. The requisition is being sent out for competitive bids. Once the competitive bids are received, the vendor will be selected and a purchase order issued.

A decision must be made concerning the addition of the X-axis motor and encoder to the comparator/microdensitometer. In this regard, the following two options are available. First, installation of the X-axis drive motor and encoder can be contracted. Second, appropriate members of our research group can visit a number of laboratories currently using microdensitometers/comparators to ascertain the type of encoder and X-axis moter which would be most suitable for our applications. This unit would then be purchased and installed by our group. Consideration of the cost and time involved in each option will dictate which alternative is selected. Visitations to these laboratories would also be extremely useful in constructing the interface between the comparator/microdensitometer and the minicomputer in the data acquisition system. We also plan to initiate the acquisition of software programs for logging data off the photographic plates and for processing and working up the acquired data on the Oklahoma State University IBM 370/158.

Initial applications of the technique of micromolecular probe distillation in conjunction with field ionization mass spectral analysis is anticipated during Professor R. D. Grigsby's scheduled visit to our laboratory this quarter.

Relative field ionization sensitivities will be determined for various saturate and aromatic mixtures and for mixtures of saturates and aromatics. Absolute sensitivities will also be measured. In order to make these measurements, a gallium frit may be incorporated into our all-glass inlet system.

Task 3 — Use of Mass Spectometer Facilities to Provide Analytical Data for Other ERDA-Sponsored Projects.

With the approval of the technical officer, Dr. Paul C. Scott, Program Manager, Fossil Energy Research, ERDA, the principal activities under Task 3 have been deferred until installation of the data acquisition system. However, this project has supported our collaborative characterization research with J. E. Dooley's Separations and Characterization Group at the Bartlesville Energy Research Center which is funded under ERDA contract No. E(34-1)-0020. The activities performed under this contract during the past quarter are summarized in Quarterly Progress Report BERC-0020-6. The present contract has also been used to support the characterization aspects of our collaborative research with Professor B. L. Crynes and his colleagues in the School of Chemical Engineering at Oklahoma State University. The tailoring of catalysts for coal-liquid processing is supported under ERDA contract No. E(49-18)-2011. The activities during the last quarter are summarized in Quarterly Progress Report FE-2011-6 Dist. Cat. UC-90d.

Work Forecast

Support of our collaborative research with J. E. Dooley's group at BERC and with B. L. Crynes' group at the Oklahoma State University shall be continued. In addition, the principal investigator shall visit the Colorado School of Mines during his visits to the Laramie and Grand Forks Energy Research Centers. The purpose of this visit is to discuss the possible development of a collaborative characterization program between our group and the appropriate individuals at the Colorado School of Mines.

References

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3) H. G. Hippe and H. D. Beckey, *Erdoel, Kohle, Erdgas, Petrochem.*, 24, 620 (1971).

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6) S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, 47, 2105 (1976).

7) See Quarterly Progress Report BERC-0020-5 submitted under ERDA contract E(34-1)-0020.

8) See Quarterly Progress Report FE-2011-6, Dist. Cat. UC-90d submitted under ERDA contract E(49-18)-2011.

9) See Quarterly Progress Report BERC-0020-6 submitted under ERDA contract E(34-1)-0020.