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

(FE 2537-11)

ABSTRACT

During the past quarter, extensive annual maintenance was performed on the mass spectrometer and ancillary equipment. The technique of micromolecular probe distillation-FI/MS was applied to the characterization of petroleum heavy ends. In this regard, the available standards for converting ion time centroids to ion m/e values in the high m/e region is inadequate.

Development of a computer method for assigning most probable formulas to precise ion masses was completed. Considerable progress was made in preparing three manuscripts describing the method. The initial phase of a project which attempts to predict relative FI sensitivities from molecular parameters was completed. The effort to develop FI/MS as a technique for analyzing saturate hydrocarbons was extended to encompass total crude oils and the saturate fractions isolated from them.

Preparation of publications describing our extensive characterization of the oils and asphaltenes from a COED coal liquid were essentially completed. The presence of numerous aromatic compounds containing two nitrogens in an anthracene oil was demonstrated. Characterization of an SRC-II coal liquid was initiated.

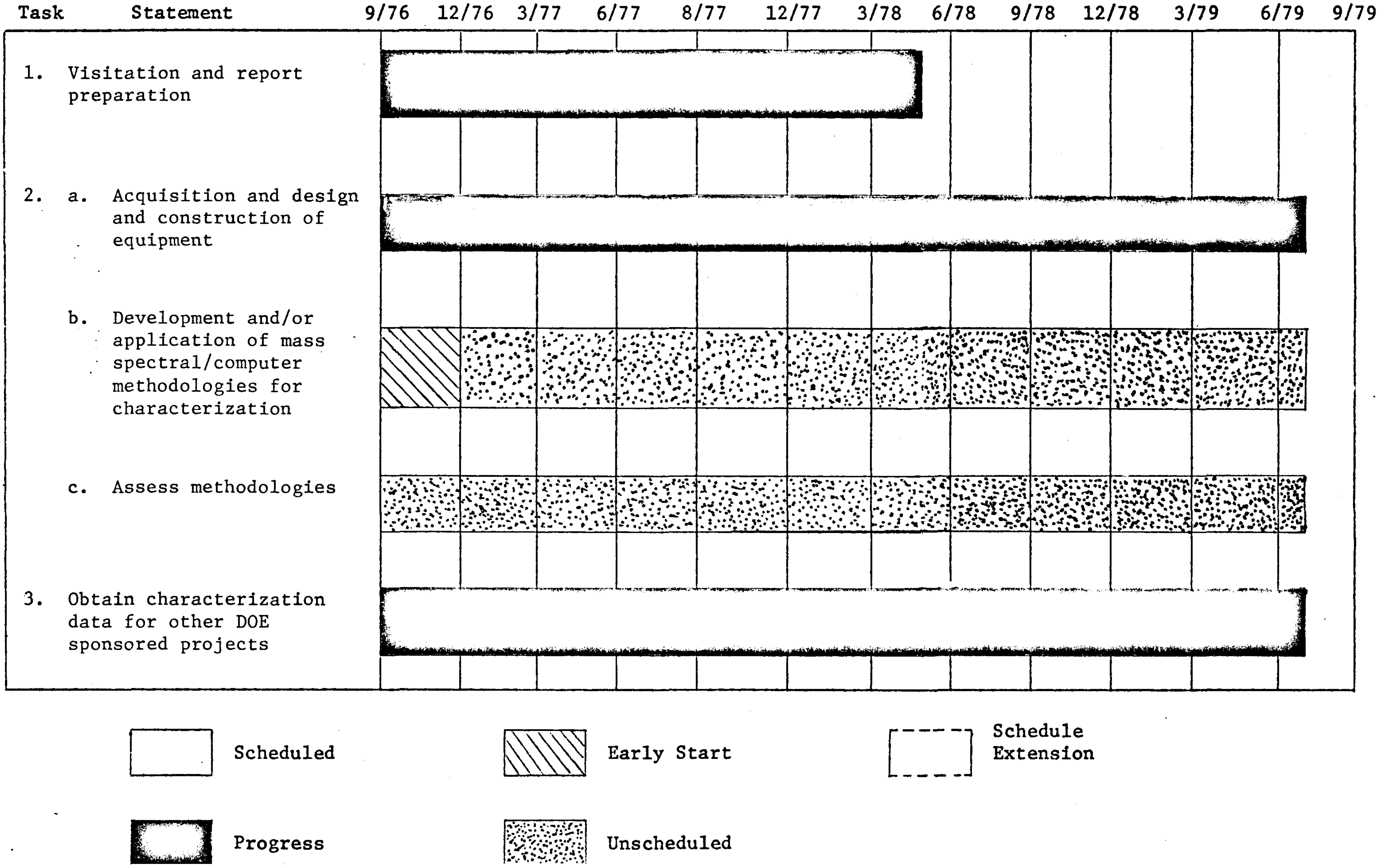
OBJECTIVE AND SCOPE OF WORK

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 spectrometric 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 DOE sponsored projects. Third, preparation of a document for DOE 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. Task 1 has been completed. Task 2 activities include: 1) installation of the DS-50S data acquisition system, 2) installation and distribution of well regulated 120V AC and an excellent electrical ground to MS laboratory instrumentation, 3) optimiation of CEC 21-110B mass spectrometer performance via major electronic modifications and maintenance, 4) optimization of system parameters for the acquisition of both low- and high-resolution mass spectral data from the CEC 21-110B in real time via the DS-50S data system, 5) implementation of communications between the NOVA 3/12 minicomputer and the IBM 370/158, 6) development of software and acquisition of hardware for implementing micromolecular probe distillation in combination with field-ionization mass spectrometry, 7) modification of the FI/EI source to operate in the field-desorption mode and construction of an apparatus for preparation of FD emitters, 8) installation of the gas chromatographic digital integrater, and 9) preparation of an initial design for an interface between the NOVA 3/12 and the comparator/microdensitometer. Task 3 activities include support of our characterization research in collaboration with J. E. Dooley's and B. L. Crynes' DOE-sponsored projects at BETC and OSU, respectively.

As of June 30, 1979, 84.7% of the total budget has been spent. This rate of expenditure is consistent with our schedule.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1. Visitation and report preparation
2. a. Acquisition and design and construction of equipment
b. Development and/or application of mass spectral/computer methodologies for characterization
c. Assess methodologies
3. Obtain characterization data for other DOE sponsored projects
Scheduled
Early Start
Schedule Extension
Progress
Unscheduled

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

This task was completed during the quarter March 30, 1978 - June 29, 1978. The document has been published by the Technical Information Center as DOE report FE 2537-7, Dist. Category UC-90d.

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 Drs. Q. G. Grindstaff, and C. S. Hwang, Ms. Michele Derrick and Messrs. P. A. Benson, N. B. Perreira, and K. N. Detwiler. Dr. Scheppele is currently on a leave of absence and is at the Bartlesville Energy Technology Center. During this period of time, Dr. Grindstaff is supervising activities of the group in the Department of Chemistry with Dr. Scheppele consulting on a regular basis.

During the past quarter extensive annual maintenance was performed on the CEC 21-110B mass spectrometer. In particular, the ion source and analyzer sections were brought to atmospheric pressure so that the electric sector, flight tube, shut-off valve between the ion source and the first field-free region, and the cold traps on the diffusion pumps could be cleaned.

The technique of computerized micromolecular probe distillation/field-ionization mass spectrometry was applied to the analysis of several GPC fractions obtained from separation of petroleum heavy ends. The fractions were found to be quantitatively volatile and the FI/MS of the distillates exhibited molecular ions ranging in mass from about 650 to *ca.* 850. At the present time, major difficulty with the method is accurate calibration of the ion time centroids corresponding to m/e values in this range. An acceptable calibration mixture does not yet exist for field ionization. Consequently, our approach has been to generate low- and high-resolution calibration files from the 70-eV EI/MS of high-boiling perfluorokerosene. Low-resolution FI/MS are then acquired on-line using an ion of known mass and the former calibration file. On-line acquisition of both low-resolution FI/MS and high- and low-resolution 70-eV EI/MS to m/e = x requires a calibration file extending to *ca.* m/e = x + 100. Unfortunately, the 70-eV EI/MS of various samples of high-boiling PFK acquired at trap currents up to 200 μA extend to only about m/e 600 at resolutions in excess of *ca.* 8000 and to about m/e 800 at a resolution of *ca.* 2000. For the petroleum heavy ends fractions, these results preclude the conversion of time centroids acquired from the low-resolution FI/MS to nominal masses and the time centroids acquired from the high-resolution 70-eV EI/MS to precise masses with sufficient accuracy. Consequently, we are exploring the suitability of other substances, such as Fomblin, as standards for conversion of time centroids to ion masses.

Our major effort (1,2,3) to develop a computer method for assigning most probable formulas to precise ion masses was completed. The method uses the approach of Guffey and Weber (4) which is based upon the Kendrick (5) mass scale. A dedicated computer acquires and reduces the high-resolution mass spectral data and a time-sharing computer processes the acquired data. In order to achieve maximum flexibility, the concept of structured programming is employed. Thus, the method can be easily tailored to meet very specific user needs and/or hardware configurations. The method consists of the following program units. Program FZM assigns formulas and specific Z values to precise ion m/e values using an existing database. Program DBG generates the database. Program XTRC sets up the precise ion m/e values obtained on-line via analog detection in the proper format for remote execution of FZM. Consequently, other programs can be developed for entering to FZM HR/MS data acquired by off-line techniques such as photoplate detection.

In order to circumvent the resource limitations of minicomputers and to take advantage of the resource capabilities of large-scale scientific computers, two versions of program FZM were developed using Fortran. One version executes on minicomputers such as the PDP 11/70 possessing *ca.* 32 K bytes of main storage, including operating-system storage, and at least one disc unit. This version of program FZM necessarily utilizes explicit program folding techniques such as overlaying and segmentation. Although capable of execution on large-scale computers such as the IBM 370/158, the resource capabilities of these machines eliminates the necessity for using restrictive programming techniques. Consequently, a second version of the program was developed for use with computers possessing at least 192 K bytes of main memory and one disc unit. Program DBG executes on either type of computer.

At the present time, program DBG generates a database for species having the general formula $(^{12}CH_2)_n H_x {}^{14}N_a {}^{16}O_b {}^{32}S_c {}^{15}N_d {}^{18}O_e {}^{33}S_f {}^{34}S_g D_h (^{13}CH_2)_i$. The specific Z value for a given species, $Z(H, N_a, O_b, S_c)$, equals $x + h$ by definition. The constraints on x are that $-53 \le x + h = Z(H, N_a, O_b, S_c) \le 2 + a + d$. This range in specific Z values was selected so that the database contains formula codes for a wide variety of species including certain nitrogenous ones such as alkyl amines which are not considered by Guffey and Weber (4). Within this constraint, the size of the database is determined by the maximum number of heteroatoms allowed in a formula, the current value is three, and the lower limit placed upon the abundances of formulas containing one or more ^{13}C, D, ^{15}N, ^{18}O, ^{33}S, and ^{34}S relative to the abundances of formulas containing the most abundant isotopes of the elements. Thus, program FZM is capable of processing HR/MS data for a wide variety of organic compounds in addition to those encountered in fossil-energy-related materials. Furthermore, program DBG can be easily modified in order to tailor the database to meet specific user needs in regard to the analysis of compounds containing either other elements or a lesser or larger sum of nitrogens, oxygens, and sulfurs or both.

The method is described in three manuscripts which have been essentially completed. One paper (6) defines inherent chemical terminology and illustrates its use, presents an overview of the computer-based mathematical terminology, and presents typical results obtained from application of the method to complex mixture analysis. Other publications present a detailed discussion of the mathematics employed, documentation of the program units, and a listing of the source programs (7) and provide a compilation of available databases (8).

Knowledge of ionization sensitivities is a prerequisite for the determination of accurate quantitative distributions from both field ionization and low-voltage mass spectra. The existing correlations of ionization sensitivities (9,10) with molecular structure are empirical. The prediction of sensitivities is thus difficult because the existing correlations are both empirical and do not encompass a sufficiently wide range of compound types. Consequently, we have been attempting to develop a correlation between relative cross sections for field ionization and fundamental molecular parameters including molecular polarizabilities, dipole moments, and ionization potentials. The initial results of this study are quite encouraging. Since the details are presently being incorporated into the M.S. thesis of Ms. M. J. Derrick, they will be reported in a subsequent report.

In order to continue the development of FI/MS as a technique for obtaining carbon-number distributions for saturates, the requisite field-ionization mass spectra were acquired for seven crude oils and the saturate fractions obtained from them. The samples were supplied by the Bartlesville Energy Technology Center. The FI/MS of the saturate fractions were converted into carbon-number distributions as a function of saturate type, the distribution of weight percents as a function of Z(H), weight percents as a function of carbon number across Z(H) series, and average molecular weights for both the +2 Z(H) series and the total sample. These results will be compared with analytical data obtained from gas chromatography and ASTM 70-eV EI/MS matrix methods. The latter analytical data are being acquired at BETC.

Work Forecast

1) Finish manuscript describing extensive modification to the CEC 21-110B in order to achieve maximum compatability with the data-acquisition system.
2) Explore the suitability of materials as calibration standards in the region of high m/e values, i.e. from m/e 600 to m/e 1000.
3) Complete three manuscripts describing the computer method for assigning most probable formulas to precise ion masses.
4) Assess status of the development of predictive correlation between relative FI cross sections and fundamental molecular parameters.
5) Pursue development of FI/MS as a technique for the quantitative analysis of saturated hydrocarbons by continuing the analysis of saturate fractions and crude oils discussed above.

Task 3 - Use of Mass Spectrometer Facilities to Provide Analytical Data for Other DOE-Sponsored Projects.

With the approval of the technical project officer, Janet L. Shultz, Pittsburgh Energy Technology Center, DOE, the principal activities under Task 3 have been deferred until installation of the data-acquisition system. However, this project has supported, in past, our collaborative characterization research with J. E. Dooley's Separations and Characterization Group at the Bartlesville Energy Technology Center. In this regard, activities during the past quarter focused on the mass spectrometric analysis of an SRC-II coal liquid. Distillation of the coal liquid at BETC produced fractions boiling in the range <200°C, 200-325°C, and 325-425°C. The 200-325°C and the 325-425°C distillates were separated at BETC into monoaromatic, diaromatic, polyaromatic/polar, acid, and base concentrates. Low- and high-resolution FI/MS were acquired for all ten concentrates in order to determine the weight percents of the various homologs in each specific Z series. The specific compound types (Z series) present in each concentrate will be determined from the high-resolution 70-eV EI/MS. To date, the requisite high-resolution 70-eV EI/MS data have been obtained for the 325-425°C monoaromatic, diaromatic, and polyaromatic/polar concentrates.

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. During the past quarter the remaining data analysis associated with our detailed characterization (11) of the oils and asphaltenes isolated from a COED liquid was completed. With the approval of the technical project officer, Janet L. Shultz, report FE-2537-10 was reserved in order to publish the complete set of experimental data acquired in this study and the associated results and conclusions. A condensed version of this manuscript will be submitted for publication in Fuel. During the past quarter, preparation of the former and latter manuscripts was essentially completed and initiated, respectively. Also a paper describing the significant results and conclusions from this study was prepared for presentation in the "Symposium On the Chemistry of Asphaltenes", sponsored by the Division of Petroleum Chemistry (12).

Feedstock and upgraded anthracene oils were previously characterized (13,14) as part of our collaborative interaction with Professor B. L. Crynes' group. The composition of the base fraction isolated from the anthracene oil was reinvestigated in order to determine the origin of the excess intensities of numerous even mass ions in its FI/MS. The presence of numerous homologs of various aromatic compounds containing two nitrogens was demonstrated as follows. Professor R. D. Grigsby at Texas A&M University subjected the base fraction to HPLC in order to produce better defined fractions. Using the technique of micromolecular probe distillation, high-resolution 70-eV EI/MS were acquired for these HPLC fractions in order to determine most probable ion formulas. These results were compared to the high-resolution 70-eV EI/MS data acquired for the total base fraction at Oklahoma State University. Both analyses indicated the presence of aromatic compounds containing two nitrogens. However, these results are not conclusive because the resolution capabilities of the 21-110B are inadequate to resolve $C_nH_{2n+Z(N_2)}N_2$ molecular ions from $^{13}CC_{n-1}H_{2n+Z(N)}N$ molecular ions for many values of Z(N) and $Z(N_2)$. However, the most probable formula assignments from these high-resolution 70-eV EI/MS were used to obtain monoisotopic FI/MS of the total base fraction from the experimental FI/MS. The weight percents of the homologs in the various $Z(N_2)$ series were calculated from the low- and high-resolution FI/MS. Conclusive evidence for the presence of numerous aromatic compounds containing two nitrogens was obtained by Dr. Thomas Aczel of the Exxon Research and Engineering Company in Baytown, Texas from the ultra-high resolution low-voltage EI/MS of the total bases acquired using an AEI MS/50. This result constitutes one of the first observation of significant numbers of N_2 compounds in products derived from coal. Consequently, the results are being prepared for submission to Fuel.

Work Forecast

1) Complete acquisition of high-resolution 70-eV EI/MS of fractions from SRC-II. Proceed with the reduction of the composite mass spectral data resulting in a characterization of the SRC-II liquid.
2) Complete preparation of manuscripts pertaining to the analysis of oils and asphaltenes from the COED liquid and the N_2 compounds in the anthracene oil.

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