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

Quarterly Report for the Period
September 29, 1977 to December 29, 1977



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# CHARACTERIZATION OF COAL-DERIVED LIQUIDS AND OTHER FOSSIL FUEL RELATED MATERIALS EMPLOYING MASS SPECTROMETRY
(FE 2537-5)


## ABSTRACT

The Data General RJE80 software has been implemented and communications were established between the Nova 3/12 minicomputer in the mass spectrometer laboratory and the IBM 370/158 computer in the campus Computer Center. To date, the communications line has been used to significantly expedite the Z-series analysis of high-resolution mass spectral data recovered from photographic plates. A program has also been written which extracts high-resolution mass spectral data, acquired directly from the mass spectrometer by the DS-50S data system, from disc in the Nova 3/12 and prepares it for remote job entry to the IBM 370/158 for Z-series analysis. This program also significantly facilitates data analysis by eliminating tedious key-punch work.

Performance of the CEC 21-110B mass spectrometer and the DS-50S data system combination has been optimized for quantitative analysis. Design of the interface between the Nova 3/12 and the comparator/microdensitometer is progressing.

Detailed investigation identified electrical problems prohibiting the attainment of optimum performance of the mass spectrometer/data system combination. The Department of Chemistry provided funds to eliminate these problems and corrective action is nearly complete.

Part I of the Task I document is being reorganized based upon comments from individuals who reviewed it. A Glossary of Terms section is being added. The remaining sections of the document are being drafted.

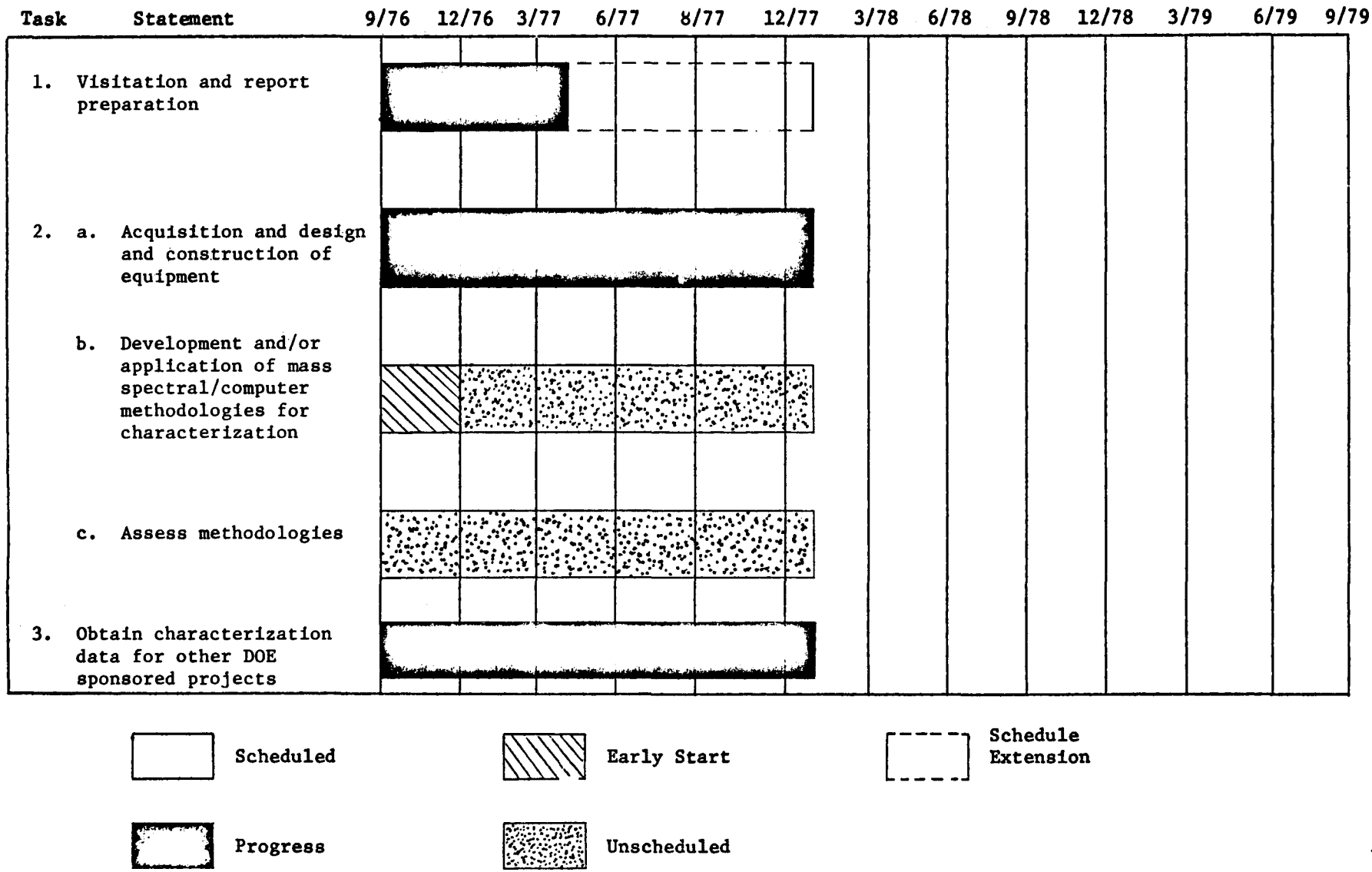
## OBJECTIVE AND SCOPE OF WORK

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 ofssil 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 the time requirements and the imperative need to be involved in Task 2 activities. However, the Introduction and Part I of the report have been completed. Part I is being reorganized based upon technical comments received from individuals who reviewed it. Based upon these recommendations a Glossary of Terms section is being incorporated into the document and rough drafts have been written for several sections of Part II. Task 2 activities include: 1) installation of the DS-50S data acquisition system, 2) receipt and installation of the gas chromatographic digital integrator, 3) implementation of communications between the Nova 3/12 mini-computer and the IBM 370/158 in the campus Computer Center, 4) optimization of system parameters for the acquisition of low-resolution mass spectral data from the CEC 21-110B via the DS-50S data system, 5) redesign of the RC network in the Nova 3/12-CEC 21-110B interface, 6) in regard to the CEC 21-110B mass spectrometer incorporation of a high-impedance operational amplifier in the magnet current power supply, optimization of the ion-beam β-focus, adequate shimming of the magnet pole pieces, and initiation of maintenance checks on all power supplies, 7) acquisition of minicomputer foreground/background capability, and 8) initial activities in regard to design of the interface between the Nova 3/12 and the comparator/microdensitometer. Task 3 activities include: 1) support of our characterization research in collaboration with J. E. Dooley's and B. L. Crynes' DOE sponsored projects at BERC and OSU, respectively.

As of December 29, 1977, 40% of the total budget has been spent. This rate of expenditure is consistent with our schedule.


Task
Statement
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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

As noted in the previous quarterly progress report (1), comments were solicited from a number of individuals concerning both the organization and content of the Introduction to the document and of Part I which is entitled "The Contribution and Importance of Mass Spectrometric Analysis to Fossil-Energy Conversion Technology". Based upon the detailed comments received from these individuals a Glossary of Terms section is being added to the document and the presentation of the subject matter in Part I is being reorganized. The organization of Part I will follow the detailed outline developed by Dr. A. L. McClellan of Chevron Research Company who reviewed the material at the request of Dr. E. J. Gallegos. Also, a limited amount of additional technical information will be incorporated into Part I. The general organization of the document will thus be as follows.

I. Introduction
II. Glossary of Terms
III. The Contribution and Importance of Mass Spectrometric Analysis to Fossil Energy Conversion Technology.
IV. The Status of the Mass Spectrometric Technique in Relation to the Characterization of Fossil-Energy-Derived Materials.
V. Recommendations.

The reorganization of II and the drafting of IV and V are in progress and would have been completed except for the extensive and necessary involvement of the Principal Investigator in resolving two major technical problems associated with Task 2 activities.

Work Forecast

Finish reorganizing section III, prepare section II, and complete drafting sections IV and V.

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 who have been participating in these activities are: Dr. T. D. Marriott and Messrs. P. A. Benson, N. B. Perreira, and K. N. Detwiler. During the quarter Dr. C. S. Hwang, Ms. Michele Derrick, and Mr. Howard Van Woert joined the project.

As previously mentioned (1) a detailed check of the ion-source, ion-accelerator, and electron-multiplier power supplies was initiated in order to reduce the electronic noise associated with the ion beam and, hence, improve

the performance of the combined mass spectrometer/data acquisition system. Initiation of these activities lead us to uncover a number of important facts which are adversely affecting system performance. Several individuals including the Principal Investigator committed an appreciable amount of time in order both to determine the origin of and develop solutions for these problems. These activities are presented in summary form because they are germane to the successful completion of Task 2 and 3 activities. Our particular version of the CEC 21-110B double-focusing mass spectrometer was not originally equipped with a peak-matching chassis. The latter unit was subsequently installed without making the necessary changes in the main-frame wiring. This situation was unfortunately not corrected by the field engineer when the mass spectrometer was reinstalled at Oklahoma State University. Furthermore, the instrument was installed at Oklahoma State using three-phase rather than single-phase alternating current and without providing a satisfactory electrical ground. The instrument was so installed apparently because of unfortunate technical advice provided to individuals associated with the installation. The net result of these facts is to reduce the performance of the regulated direct-current power supplies and limit performance of the mass spectrometer especially when combined with the data acquisition system. Indeed, it seems surprising that resolutions up to 22,000 have been routinely achievable and that good ion-beam stability has been obtainable. The Department of Chemistry has authorized the expenditure of funds in order to supply the mass spectrometer laboratory with single-phase 240 V alternating current and an electrical ground. The design for these modifications, which are essentially complete, is as follows. A 25 kVA isolation transformer will supply two 120 V lines with respect to the center tap of the transformer secondary. A 4' x 5' x 1/16" copper plate buried *ca.* 5' in wet soil and connected to the mass spectrometer laboratory by a 4" x 1/4" copper strip constitutes the laboratory ground. Copper to copper connections both to the plate and along the strip are via copper bolts. Each junction is sealed using a noncorrosive epoxy resin. Single-phase 120V alternating current will be supplied to the critical power supplies in all instruments in the laboratory; power will be supplied to components such as diffusion and mechanical pumps from existing 3-phase alternating current. The various instrument grounds will be connected to the terminal plate on the copper strip in a fashion which experimentally minimizes the generation of ground loops. Outside technical assistance will be obtained in distributing single-phase alternating current to the various instruments, in properly grounding each of the instruments, and to optimize performance of the double-focusing mass spectrometer. The individual has been selected based upon detailed discussions between the Principal Investigator and appropriate individuals associated with both industrial and governmental mass spectrometer laboratories.

Communications were established on December 21, 1977 between the Nova 3/12 minicomputer in the data acquisition system and the Oklahoma State University IBM 370/158 computer. Task completion required the development of effective interactive communications between various individuals associated with Data General, IBM, the Oklahoma State University Computer Center, the modem manufacturer, and the project. A disc containing the Data General RJE80 software was received from Massachusetts Computer Associates (1). Initial attempts to implement RJE80 were unsuccessful. Consultations with individuals at Data General confirmed that several additional modifications to the software were required and the necessary patches were added by individuals in the Tulsa

office of Data General. Further attempts to establish communications indicated the presence of difficulties associated with the hardware. Correct performance of the modems at each end of the communications line (1) was ascertained by verifying the input/output signals with the manufacturer and by using them in a functioning communication line to the IBM 370/158. The hardware problem was resolved upon 1) removal of the W5 strap from the communications board in the Nova 3/12 and grounding out the signal from the Nova 3/12 communication chassis used for telephone ring-up communication lines. Information supplied by both Data General and IBM was used by individuals in the Computer Center and in the research group to establish correct system parameters for both the Nova 3/12 and the IBM 370/158 computers. Our initial use of the communication line in regard to the mass spectrometric characterization of fossil energy derived materials is described below.

A program was developed (2) which reads carbon-12 masses obtained from high-resolution mass spectra data, converts them to the corresponding Kendrick ($CH_2 = 14$) molecular weights (3), and assigns molecular formulas and Z values consistent with the general formula $C_NH_{2N+Z}N_aO_bS_c$ to each Kendrick mass within a specified tolerance. The computational methods to do this are based on the tables previously developed by Guffey and Weber (4). The program is named MZF since the output consists of masses, Z values, and molecular formulas; MZF resides on disc in the Computer Center. The input carbon-12 masses are obtained from high-resolution mass spectra recorded either on photographic plates or as the time dependent output of the electron multiplier.

At the present time the high-resolution mass spectral data retrieved from the photographic plates using a comparator/microdensitometer consist of the line positions corresponding to the m/e values of the ions in the mass spectrum of the sample plus the reference perfluorokerosene. The line positions and the m/e values of the ions from perfluorokerosene are punched on computer cards. The card reader and the Nova 3/12 computer in the mass spectrometer laboratory and the communications line are used to introduce the data to the IBM 370/158 which calculates precise m/e values for the ions in the mass spectrum of the sample. These ion masses are then processed through MZF and the results are returned to the mass spectrometer laboratory via the communications line and printed on the printer/plotter. The system possesses excellent turnaround time, i.e., the elapsed time from initiation of data transmittal to receipt of processed data is only several minutes. Efficiency will be further increased when the comparator/microdensitometer is interfaced to the Nova 3/12; see below.

The Nova 3/12 minicomputer in the data acquisition system acquires the time dependent output of the electron multiplier and converts the acquired data to ion m/e values and associated ion intensities. For operation of the mass spectrometer at high resolutions, it is clearly desirable to transmit the so acquired precise ion masses via the communications line to the IBM 370/158 for processing through disc-stored program MZF. As a means to do this, a program which sets up the Nova 3/12 acquired high-resolution mass data and the job control language (ICL) was developed. Both the flexibility and ease of operating the program have been demonstrated. The algorithm and operating procedure are described below.

The program was written in Fortran IV and is implemented to AEI's DS-50S system software. It was decided that the program must meet the following criteria. First, the program must be able to handle multiple sets of data. Second, the program must allow the operator to select certain type of masses

to be extracted, such as even masses and mass range. Third, all undesired masses must be automatically excluded.

The algorithm involved is rather straight forward. The program first requests the following information from the operator: (1) scan names, (2) the mass range to be considered, (3) the file name assigned to the output, (4) the parity code which determines whether only even masses or only odd masses or both even and odd masses are to be included. As soon as these data are obtained, the program writes the JCL and opens the mass file associated with the first scan name. If the mass file does not exist, the program simply ignores it and opens the mass file of the next scan. Otherwise, the program writes the scan name and parameters which are required by the Z series program. Subsequent to this, the mass data are read peak by peak and converted from AEI's internal format into Data General's floating point format. Special peaks such as PFK reference peaks, lock masses, and dummy masses are excluded prior to the conversion. The exact mass is written out if it meets the specified parity and mass range. When all the peaks in the mass file have been processed the program closes current mass file and proceeds to the next scan until all the scans are completed. The flow chart of the algorithm is shown in Figure 1.

The program is initiated by typing USRA. The following sample dialogue demonstrates the simplicity of the operating procedures.

```
USRA(CR)
SCANS:  GULFR4.6 (CR)
RANGE:  200-300 (CR)
REPORT DEVICE:  DPOF = NEWSET.01 (CR)
MASS PARITY (EVEN = 0, ODD = 1, BOTH = 2) = 0 (CR)
R
```

Note CR denotes the operation of carriage return.

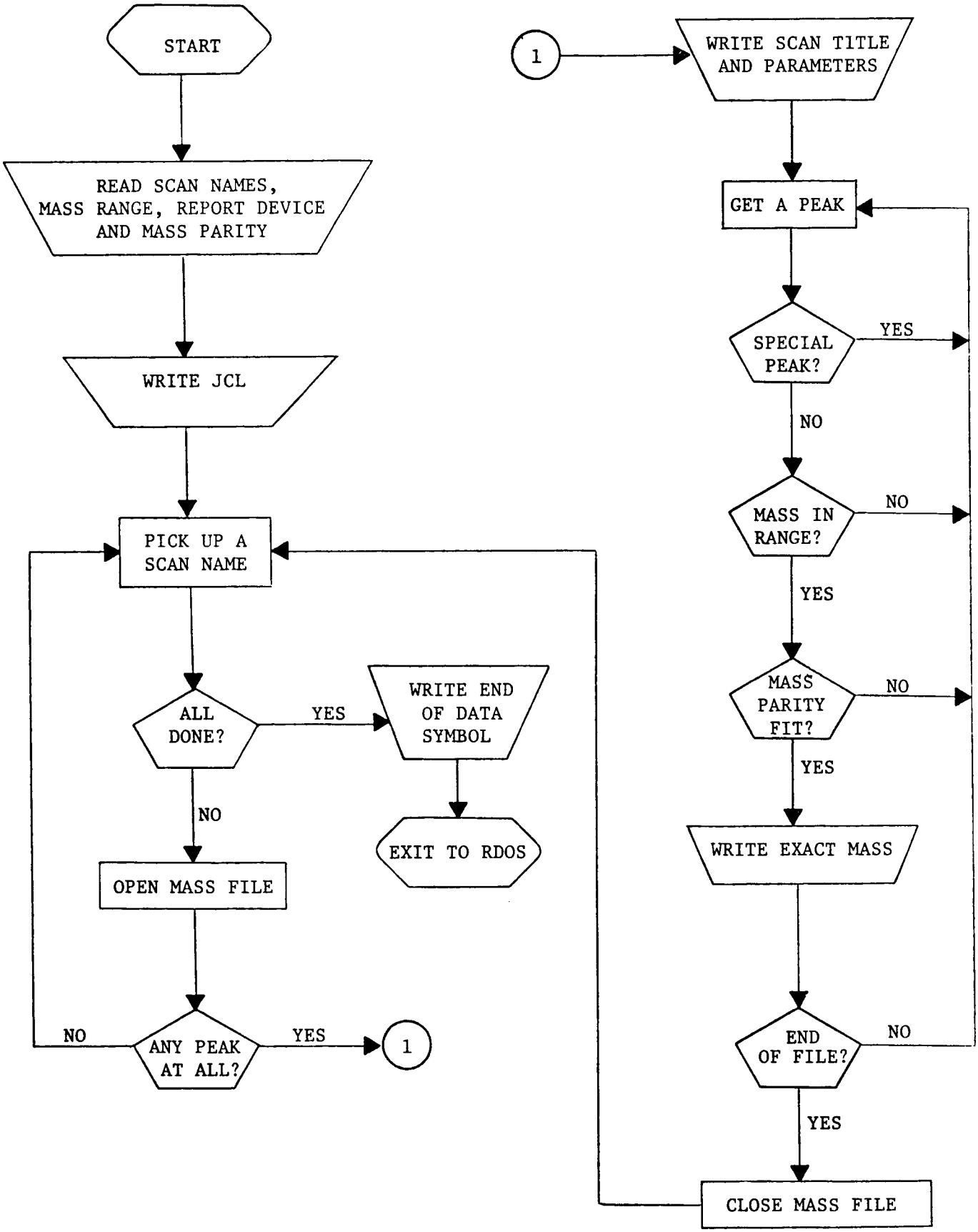
After the ready sign appears on the console the disc file, NEWSET.01, may be transmitted anytime using Data General's RJE80.

Dr. T. D. Marriott attended a DS-50S Users Course, October 11-14, 1977 at Union Carbide Laboratories in South Charleston, West Virginia under Dr. Keith Compson on DS-50S software and Mr. Ged Tyror on the KRATOS/AEI mass spectrometer interface and interface diagnostics. Methods of using the AEI interface diagnostic program DIAGN.SV to check and adjust the calibration of the high- and low-speed analog to digital convertors were demonstrated. These calibration checks were shown to be needed to verify that the interface is collecting accurate mass spectrometer data.

The DS-50S software for mass spectrometer data collection and processing and the associated Data General Corporation RDOS file maintenance software were covered in detail including:

1. setting tunefile parameters.
2. configuring data acquisition program files (online and offline processing).
3. data acquisition (DATAC).
4. calibration files (calculation and use in time-to-mass conversion).
5. data processing and display (QUAN reports, ATOM reports, etc.).

FLOW CHART


START
READ SCAN NAMES, MASS RANGE, REPORT DEVICE AND MASS PARITY
WRITE JCL
PICK UP A SCAN NAME
ALL DONE?
YES
WRITE END OF DATA SYMBOL
EXIT TO RDOS
NO
OPEN MASS FILE
NO
ANY PEAK AT ALL?
YES
1
1
WRITE SCAN TITLE AND PARAMETERS
GET A PEAK
SPECIAL PEAK?
YES
NO
MASS IN RANGE?
NO
YES
MASS PARITY FIT?
NO
YES
WRITE EXACT MASS
END OF FILE?
NO
YES
CLOSE MASS FILE

6. RDOS commands (DELETE, PRINT, etc.).
7. the VERIFY program for emergency file maintenance and repair.
8. display editor for interactive graphics on Tektronix video display.

The information acquired in this course was used to set up low-resolution tunefiles and the quantitative accuracy of the acquired ion abundance data was tested by calculating field-ionization relative gram sensitivities for the components of mixtures of known composition. Table I presents the composition and relative gram sensitivities for a sample called Computer Test Mixture #1. This sample was run on our CEC 21-110B mass spectrometer at a magnet scanning rate of 45 sec/decade. Columns 4 and 5 present relative abundances obtained by averaging the values from 10 scans both by hand and using the DS-50S PKAVG.SV, respectively. Agreement is excellent. The relative abundances in column 4 were used to calculate relative gram sensitivities in column 6. Comparison of the values in columns 6 and 7 reveals that the present relative sensitivities are in good agreement with previous values.

These low-resolution field-ionization mass spectra were collected in the presence of the lockmasses acetone (m/e 58) and benzene (m/e 78) which were used to convert the time centroid files to nominal mass files. The calibration files used in the time-to-mass conversion for the FI scans were created with the CEC 21-110B operated in the EI-mode using high-boiling perfluorokerosene. The magnet scanning stability is apprently quite good in the low-resolution mode at the present time since a calibration file created November 30, 1977 is still successfully in use for time-to-mass conversion in the first week of January, 1978.

A Task 2 activity involves interfacing the Grant comparator/microdensitometer to the Nova 3/12 minicomputer and developing software to permit computer acquisition of the ratio of the intensity of the light beam incident on the photographic plate to the intensity of the light beam transmitted by the photographic plate as a function of distance along the plate. The interface module reflects the choice of X-axis drive motor and encoder and associated control units. Technical information concerning the latter items was acquired from a number of vendors. One vendor supplies a encoder/lead-screw-driver combination which is microprocessor controlled. This vendor has graciously offered to supply us with a unit in order to verify that the motor has sufficient torque to drive the lead screw and with technical information in regard to interfacing the microprocessor and the Nova 3/12. Consideration is being given to the components required in the interface between the photomultiplier tube in the comparator/microdensitometer and the auxiliary ADC board in the Nova 3/12.

A manuscript describing our detailed investigation (5) of the relative sensitivities for the field ionization of saturated hydrocarbons both in the absence and presence of aromatic compounds is being drafted. As part of this endeavor relative sensitivities were determined for additional compounds and redetermined for several of the compounds.

## Work Forecast

1) Complete electrical modifications in mass spectrometer laboratory and perform detailed maintenance on CEC 21-110B double-focusing mass spectrometer

TABLE I

COMPUTER TEST MIXTURE #1

| Nominal Mass | | wt. % | Relative[a] Abundance | Relative[b] Abundance | Relative Sensitivities | |
|---|---|---|---|---|---|---|
| | | | | | Present $S_g/S_{106}$ | Previous[c] $S_g/S_{106}$ |
| 210 | 2-hexyl-5-propylthiophene | 11.8 | 33.7 ± 1.7 | 33.5 | 0.65 | 0.62 |
| 202 | fluoranthene | 5.8 | 24.0 ± 2.7 | 23.6 | 0.93 | 0.89 |
| 192 | 4-methylphenanthrene | 6.0 | 24.3 ± 0.9 | 24.5 | 0.92 | 0.84 |
| 186 | octahydrophenanthrene | 17.9 | 57.8 ± 2.7 | 57.5 | 0.73 | 0.82 |
| 178 | phenanthrene | 8.3 | 37.0 ± 1.7 | 36.8 | 1.01 | 0.97 |
| 156 | 1,6-dimethylnaphthalene | 9.9 | 46.7 ± 2.9 | 46.4 | 1.06 | 0.98 |
| 142 | 1-methylnaphthalene | 17.6 | 80.1 ± 3.2 | 79.8 | 1.03 | 0.95 |
| 106 | ethylbenzene | 22.6 | 100 | 100 | 1.00 | 1.00 |

[a] Average of ten scans, deviations are standard deviations.

[b] Calculated by PKAVG.SV over ten scans of TMXT45.MS.

[c] S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, N. B. Perreira, *Anal. Chem.*, 48, 2105 (1976).

2) Optimize performance of mass spectrometer/data acquisition system combination when former is operating at high resolutions.

3) Interface direct introduction probe temperature controller to auxiliary ADC input board of Nova 3/12.

4) Develop programs for acquiring probe temperatures.

5) Commense development of programs to allow transmittal of both ion intensities and probe temperatures from Nova 3/12 to IBM 370/158.

6) Place programs for processing ion intensities as a function of temperature on disc in the Computer Center.

7) Continue development of interface between Nova 3/12 and comparator/ microdensitometer.

8) Implement foreground/background.

9) Continue development of field-ionization mass spectrometry as a technique for quantitative analysis and attempt initial acquisition of field-desorption mass spectra.

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

With the approval of the technical officer, Dr. Paul C. Scott, Program Manager, University Programs, DOE, 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 DOE contract no. EY-76-S-02-0020-A001. The activities performed under this contract during the past quarter are summarized in Quarterly Progress Report BERC-0020-10. 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 DOE contract no. EX-76-C-01-2011. The activities during the last quarter are summarized in Quarterly Progress Report FE-2011-10, Dist. Category UC-90d.

## Work Forecast

Support of our collaborative research with J. E. Dooley's group at BERC and with Professor Crynes' group at Oklahoma State University shall be continued. We plan to complete the acquisition of high-resolution electron-impact mass spectral data and low-resolution field-ionization mass spectral data for fractions submitted by Dr. Dean Dickerhoff and Mr. N. W. Furlong of the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado. The research at CSM is supported by DOE under contract no. E-49-18-1225.

## References


1) Quarterly Progress Report FE 2537-4, Dist. Category UC-90d submitted under DOE contract EX-76-S-01-2537.

2) Quarterly Progress Report BERC-0020-9 submitted under DOE contract EY-76-S-02-0020-A001.

3) E. Kendrick, *Anal. Chem.*, 35, 2146 (1963).

4) F. D. Guffey and J. H. Weber, "A Tabular Method for Obtaining Empirical Formulas from High-Resolution Mass Spectral Data; (Report of Investigations, Laramie Energy Research Center, Laramie, Wyoming).

5) For preliminary reports see: a) Quarterly Progress Report BERC-0020-8 submitted under DOE contract EY-76-S-02-0020-A001; b) Quarterly Progress Report FE 2537-4, Dist. Category UC-90d submitted under DOE contract no. EX-76-S-01-2537; c) T. D. Marriott, C. S. Hsu, G. J. Greenwood, K. N. Detwiler, P. A. Benson, G. M. Stewart, N. B. Perreira, and S. E. Scheppele, Proceedings 25th Annual Conference on Mass Spectrometry and Allied Topics, 142 (1977).

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