⊕EPA
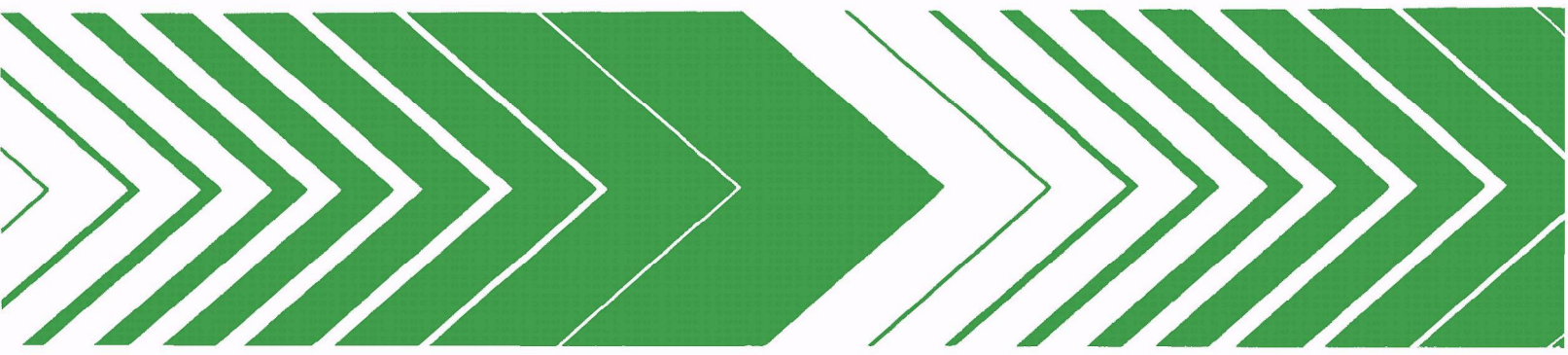
Computer Program for Reducing Mass Spectra Data from GC/MS Systems

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COMPUTER PROGRAM FOR REDUCING MASS SPECTRAL DATA
FROM GC/MS SYSTEMS

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ABSTRACT

Existing computer programs for deconvoluting mass spectrometry data derived from gas chromatography/mass spectrometry/computer systems were evaluated, and the most efficient method was introduced unto an EPA UNIVAC computer. The program chosen was that reported by Rindfleisch and his co-workers at Stanford University. The accompanying program listing is included. The Rindfleisch program was tested with both standard runs and environmental samples. Sample components were successfully identified by an independent computer search program with an accuracy approaching 80%.

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ABBREVIATIONS

GC/MS	-	Gas Chromatography/Mass Spectrometry
TIC	-	Total Ion Current
A/D	-	Analog to Digital
MS	-	Mass Spectrometry
TUCC	-	Triangle University Computation Center
GC	-	Gas Chromatograph(y)
R	-	Correlation Coefficient
H	-	Hit
M	-	Miss
I/O	-	Input/Output

SECTION 1

INTRODUCTION

Gas Chromatography/Mass Spectrometry (GC/MS) is an analytical method which has the potential capability of allowing the total automated identification of a complex mixture of pollutants. Implementation of such a technique depends on the availability of two types of new technology. The first, the automatic acquisition and storage of fast scan low resolution mass spectrometry data, has been available for some time. The first GC/MS system involving the continuous recording of mass spectral data from a mass spectrometer operating in cyclic mode was first reported by Hites and Biemann in 1968.[1] At the present time these systems are commercially produced by many manufacturers.

The availability of computer programs for the analysis of this kind of data is at present still very limited. Although software development in this field constitutes a very active research area (roughly 100 papers are published yearly), very few integrated systems have yet been developed which are generally useful. This is in part due to the large variety of computer types, each with its own individual characteristics, but more importantly due to a general unavailability of broad based algorithms with an effective philosophy of approach. As a result, the vast majority of mass spectral runs are still being analyzed by hand.

The problem of the development of a generalized system for data analysis has two aspects. The first is how to separate mathematically the raw mixed spectra into well resolved components. The second is to assign a chemical structure to each resolved spectrum. Several approaches have been tried concerning the second problem, and one based on the pioneering work of Grotch[2] had been successfully implemented and realized in the form of a library search program now resident at the RTI Mass Spectrometry Facility prior to this project. The early results of this search program however, had not been totally satisfactory, usually for the reason that the input spectra were not

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sufficiently "clear", to allow unique identification. This problem was in large part alleviated by combining the search algorithm with an appropriate cleanup procedure. The implementation of each of these two stages and their effective combination turned out to enhance the capabilities of the entire system.

After a prototype system was developed which was shown to be effective, the CLEANUP programs which were developed were adapted to the EPA environment. Since manipulation of large data bases are much more easily accomplished in a large computer, it was felt that this process was best carried out by adapting data acquired using EPA's INCOS data system and processing them on a large computer. This approach had the dual advantage of making the programming effort much simpler, since core size limitations did complicate the programming, and in addition the processing could be accomplished independently, thus freeing the INCOS system to do other work. Again, the fact that programs were written in standard FORTRAN facilitated their transfer to the EPA UNIVAC computer.

Completion of the project by delivery of the program and its documentation to the contracting agency, is effected with this report and the accompanying listings (Appendix 1).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The work accomplished under this contract can be divided into four parts: (I) a literature search to determine the most effective algorithm for deconvolution of mass spectra; (II) implementing that algorithm on an existing computer and performing detailed tests of its efficiency, both from a chemical and machine standpoint; (III) making the program operational on the EPA UNIVAC computer installation using for input a tape created using the INCOS data acquisition system; (IV) making the necessary documentation and source code (Appendix 1) available to the contacting agency.

Three techniques were considered in Phase I: background subtraction, mass max analysis, and peak profile analysis. The peak profile analysis proposed in a recent article by Rindfleisch (Appendix 2) was ultimately chosen because of its demonstrated effectiveness in existing systems (the CLEANUP program) and because it incorporated the notions of background subtraction and mass max analysis as a starting point.

Once the Rindfleisch algorithm was chosen, the task of implementing that algorithm on the TUCC 370 was undertaken. First, a detailed study of the published algorithm was made in order to gain a better understanding of what was involved and to determine if improvements were necessary. Next, a copy of the Rindfleisch program modified to run on an IBM 370 was obtained through the cooperation of a group of chemists at the NASA Ames Air Force Base. This copy was then modified to run in a batch environment at TUCC and was subjected to extensive testing, both from a machine and chemical standpoint. This included running the program under the WATFIV compiler to insure program accuracy and machine independence, followed by testing with data acquired by a VARIAN CH-7

mass spectrometer. The test data consisted of three brominated standards, followed by fifteen runs involving a wide variety of environmental samples. The RTI library search program was used throughout to evaluate the output from CLEANUP. The laboratory standards were all correctly identified and correct identifications, approaching 80% were obtained on some environmental samples. In addition, some of the CLEANUP input parameters were studied in order to determine optimum settings.

Phase III, making CLEANUP operational in the EPA environment, consisted of three parts: obtaining a successful run of INCOS test data supplied by EPA on the TUCC 370, obtaining a successful run on the same data using a version of CLEANUP adapted to run on the EPA UNIVAC computer, and finally verifying that the output tape was compatible with the contracting agency's INCOS data acquisition software and yielded plausible output spectra.

This report, together with the accompanying listings and the installing of CLEANUP on the UNIVAC comprise the completion of Phase IV of this project.

It is now necessary to carry out a thorough testing of the programs to determine what conditions and sets of parameters must be used to obtain optimal results. The principles used in developing the software are sound, however, the programs need to be tuned to fit the acquisition conditions. Some attention should be given to control studies using known mixtures, because these give the best opportunity for evaluation of the system. A statistical evaluation of the results, especially when compared with other methods, would be very profitable.

SECTION 3

LITERATURE SEARCH OF EXISTING DECONVOLUTION METHODS

Phase I of this contract consisted of a literature search to consider available alternatives for the treatment of mass spectral mixtures, and thus arrive at a best method for deconvolution. Three general avanues of attack were examined: background subtraction, mass max, and peak profile analysis.

BACKGROUND SUBTRACTION

The technique of background subtraction is basically as follows. In its simplest form, a spectrum from either an unknown GC run or some blank run is chosen as a "background" spectrum. This spectrum is then subtracted from the unknowns within the run, and the resulting difference spectra are used for mass spectral identification.

In a slightly more refined version of the technique, the background spectrum is determined manually by visual inspection of a raw total ion current (TIC) plot, and in some instances several background spectra are chosen for use in different ranges of the chromatogram.

The difficulties associated with this approach are fairly obvious. Background spectra are not constant, either qualitatively or quantitatively. Thus, what constitutes the background in one section of the run may be very different from that in another. Additionally, background peaks arising from contaminants such as column bleed change in intensity especially during temperature programmed runs.

Thus the question of how the background subtraction is to be carried out is very difficult to answer. Even the mechanics of the subtraction can be done in a number of ways. Several unsophisticated schemes exist in which the background spectra are subtracted, peak for peak, from the raw digitized unknown. Invariably, some spectra are undercorrected, while in others, real data is eliminated from the output, making identification very difficult,

either by hand or by machine. Human interpreters often prefer to look at raw data over background subtracted, since they can learn to ignore certain peaks without the removal of key unknown peaks by a clumsy program.

More sophisticated approaches have been tried wherein only a fraction of the background spectrum is subtracted. The problem of course, is to determine the proper size of the fraction.

All in all the background subtraction approach was eliminated since it is not sufficiently flexible, can give erroneous results, and lacks a way in which a consistent algorithm can be proposed for automatic processing.

MASS MAX ANALYSIS

A second and more sophisticated approach to mass spectral deconvolution has been taken by Biemann and co-workers.[3] This approach makes use of the principle that when a compound elutes from a GC column and is analyzed by continuous scan MS, the ions of each component show maximum intensity at some mean elution time.

The algorithm chosen, then, searches through each single ion trace for points of maximum intensity. The deconvoluted spectra are then defined as that collection of ions which have shown an intensity maximum within a given time window.

This approach was designed to allow the separation of mixtures of unknowns which are not sufficiently resolved to show individual TIC peaks, but which can be distinguished by the presence of single ion maxima which are not influenced by other ions not present in that particular unknown.

This idea is sound, and in fact, constitutes the first part of the Rindfleisch[4] procedure, described below. The procedure is very rapid and has actually been incorporated into other commerically available deconvolution software systems.

The program is deficient because it does not take into account a number of facts.

1.   If a given ion shows a maximum at one point, it does not by any means guarantee that this ion will <u>not</u> be present in the other component.

2. If, as often occurs, an ion is present in both components in approximately equal amounts, the observed maximum may occur between the maxima of either component and be missed entirely by the system.

3. The technique does not take into account contributions from background noise or column bleed, and treats each ion in an all or nothing manner, and therefore cannot get a proper estimate of the intensity of peaks which derive from more than one source.

The method seems to have some merit for the purpose of identifying the presence of unresolved multiplets. However, it cannot accurately predict the actual spectra, and because of the deficiencies mentioned in the previous paragraphs, sometimes fails entirely, showing specious peaks, or missing multiplets.

PEAK PROFILE ANALYSES

The algorithm for the CLEANUP program herein described was originally due to Rindfleisch and co-workers at Stanford.[4] Their program was part of an integrated GC/MS data reduction system which ran on a PDP-11/20. Following is a detailed description of the elements and mode of operation of this program. This information was gathered from the published work on the subject as supplemented by our copy of the listings and other documentation.

Raw spectra output from GC/MS systems differ from the library spectra of pure components for at least three definable reasons. CLEANUP attempts to correct mathematically these spectra in three distinct ways, corresponding to these known error sources. These are 1) Background noise and column bleed, 2) Signal saturation, 3) overlapping peaks. We will call the three portions of the program dealing with these problems Tasks 1, 2, and 3.

Errors arise for the following reasons. Superimposed on the eluant spectrum there will always be a certain constant level of background noise, and in addition other extraneous signals which normally rise slowly with increasing column temperature due to the elution of some of the liquid phase of the column. Task 1 is concerned with the distinction between the origin of these kinds of signals. Task 2 tries to reconstruct the actual intensity level of peaks which are so strong that they have exceeded the range of the A/D convertor. This is the problem of peak saturation. Task 3 is the reconstruction of peak intensities of two or more compounds which elute so closely to one another that their

mass spectral peaks are intermixed. The guiding principle which allows the CLEANUP program to function is that it uses information both in advance and after a particular scan to distinguish between real peak unknown information and extraneous data. Such issues as column bleed detection, doublet resolution, background detection, etc. are defined in the context of a region of scans rather than a single scan. The CLEANUP program makes use of fourteen MS scans in core at any one time (Figure 1). For tasks 1 and 2, only the seven innermost scans are used. For some details (e.g., background estimation), all 14 scans are needed. For multiplet resolution, all 14 scans are used. The processing proceeds from the beginning of the run to the end in a single pass always using 14 spectra. The spectrum window in core is progressively updated by the addition of one spectrum from one end and the dropping of one spectrum from the other.

The CLEANUP algorithm can be divided into stages from a programming point of view. The first stage is the examination of the spectral window and determine whether or not an eluant is present at all. When a peak, or group of peaks is detected, then tasks 1, 2, and 3 can be undertaken to improve the quality of the raw data. The detection process is accomplished as follows: The program looks at a window seven scans wide as the input spectra move through the fourteen spectrum window in core. For each of the 411 masses in the seven scan window (each scan covers masses 40 to 450 the program does a primitive check to see if the window contains a simple maximum (Figure 2). As maxima are detected, histogram of the frequency of "singlet" maxima is created. Data are ignored if there are any "lumps" (indicating a doublet) or if peak saturation is observed anywhere in the window (Figure 3). In addition to the histogram of the number of occurrences of maxima (Figure 4), a record of a slightly modified total ion current is kept (Figure 5), i.e, once a singlet maximum is detected, a rudimentary approximation to column bleed and background is subtracted (corresponding to the lowest value in the 14 a.m.u. window), the ion current at the maximum is estimated via interpolation, and the resulting ion current is added into a peak amplitude record. When an appropriate number of scans have passed through the window (the statistics are updated continuously) a decision is made on the basis of the number of maxima observed and the total amplitude of those maxima whether an eluant is present. It should be mentioned here that at this

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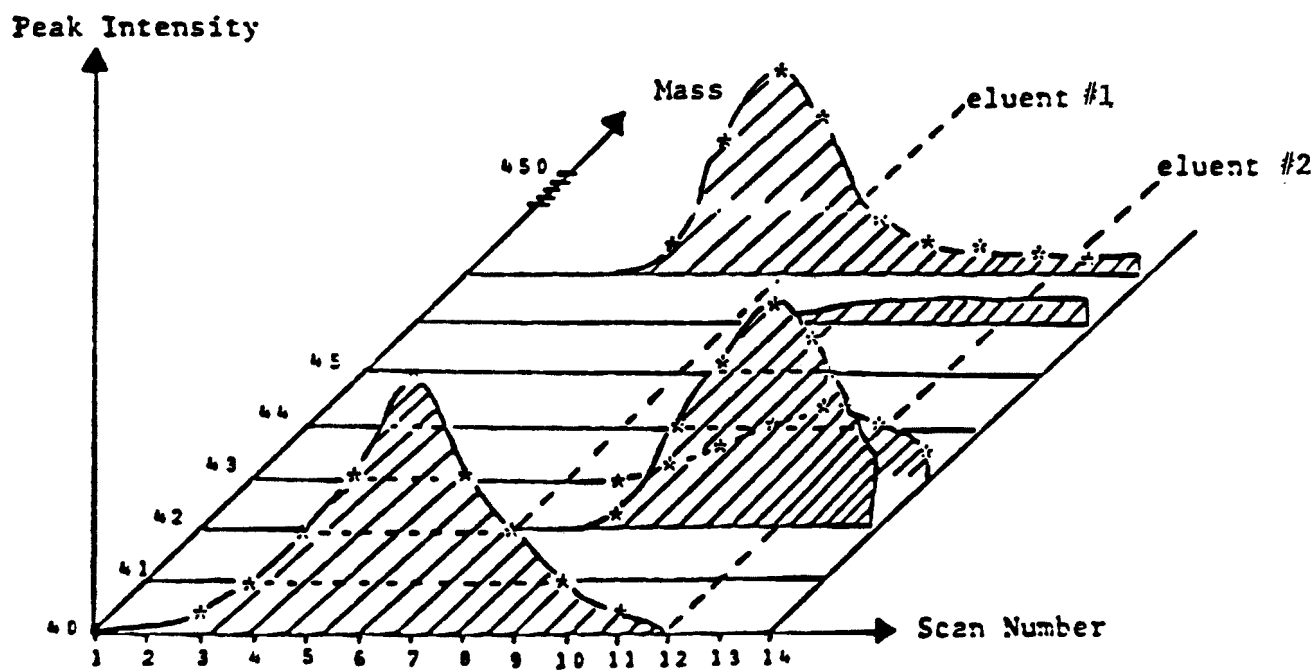
Figure 1.   Schematic representation of 14 scan window for Masses 40-450 in core - a typical case.
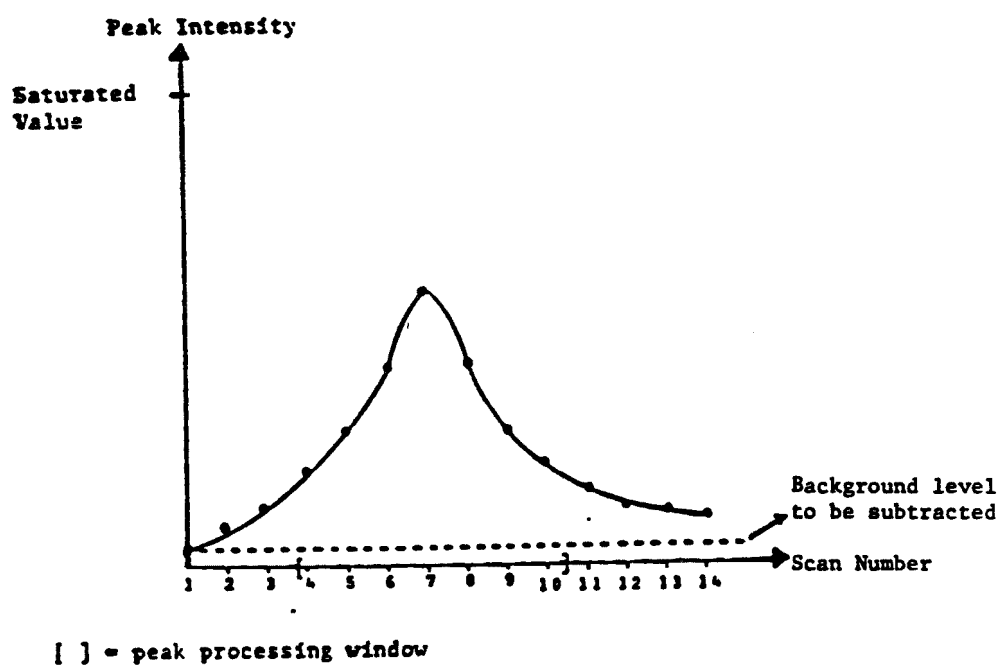
Figure 2. A typical singlet peak model for a given mass.
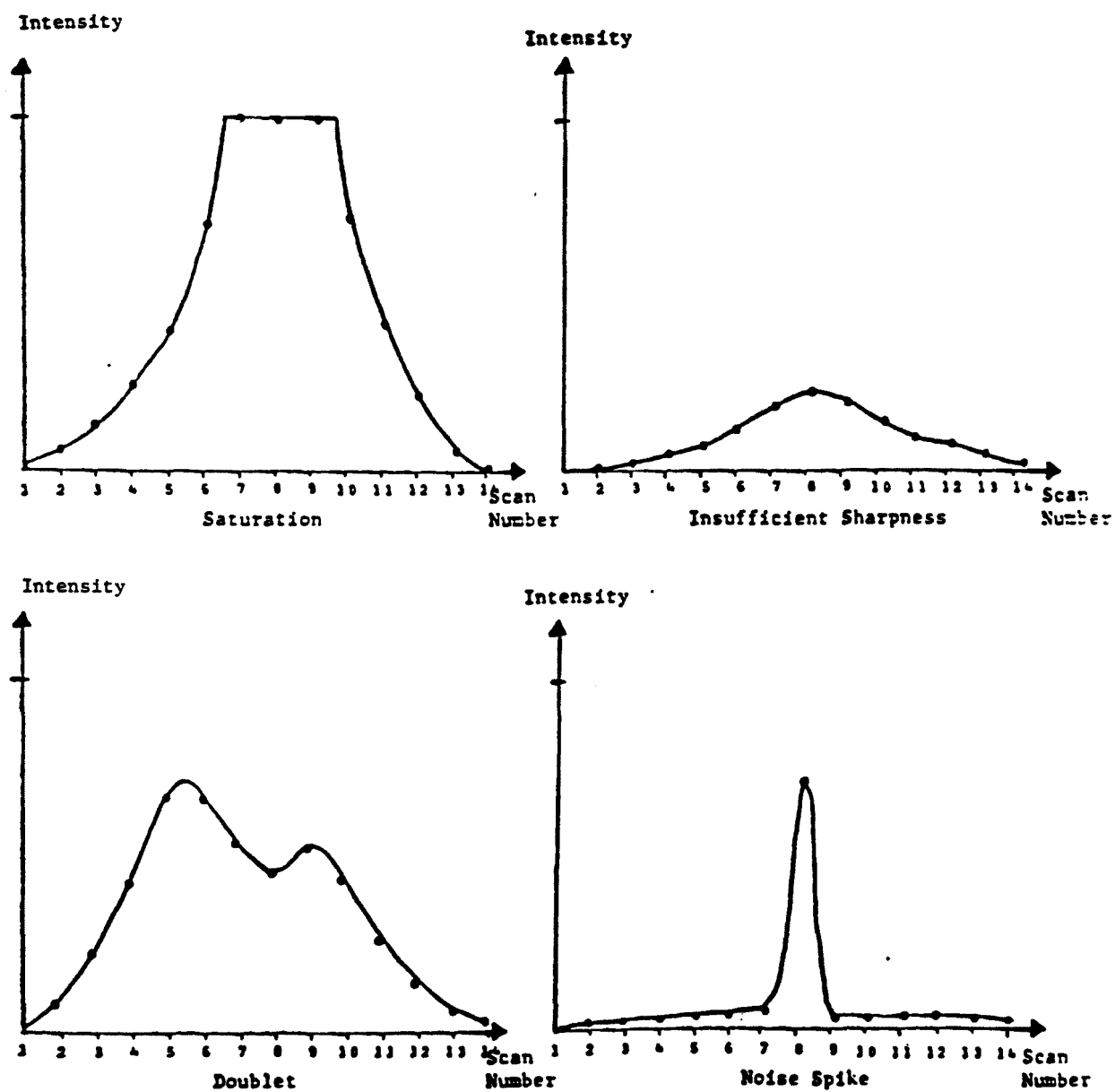
Figure 3. Various types of situations which do not qualify in histogram calculation.
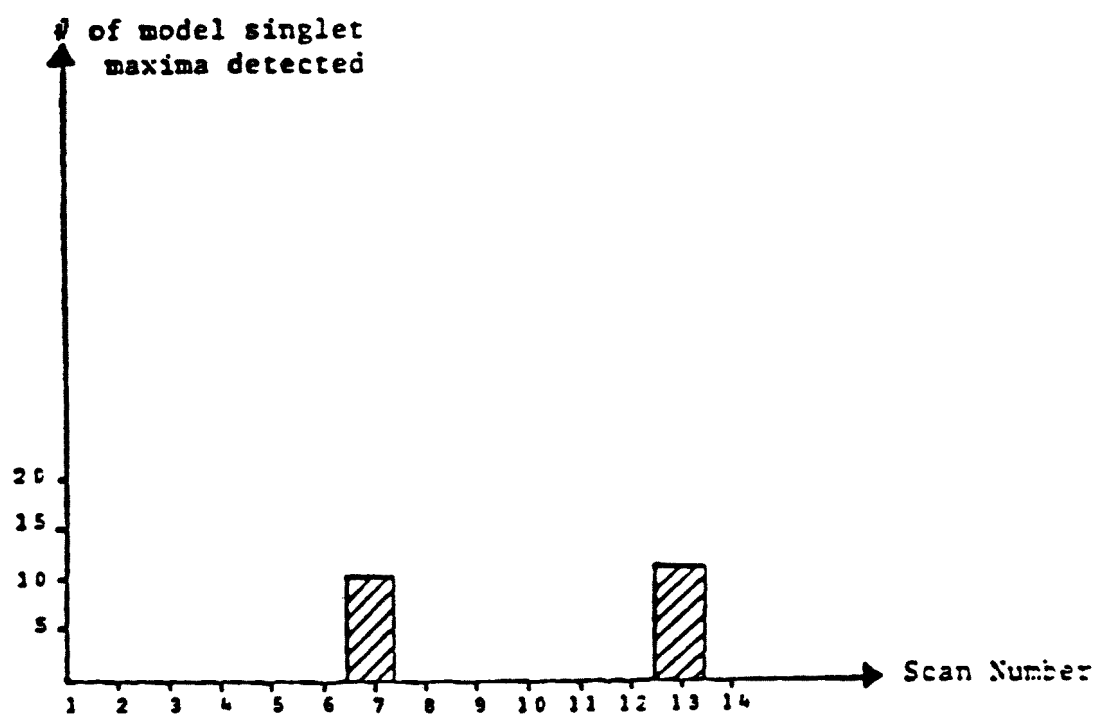
Figure 4. Peak detection histograms for sample processing window of Figure 1.
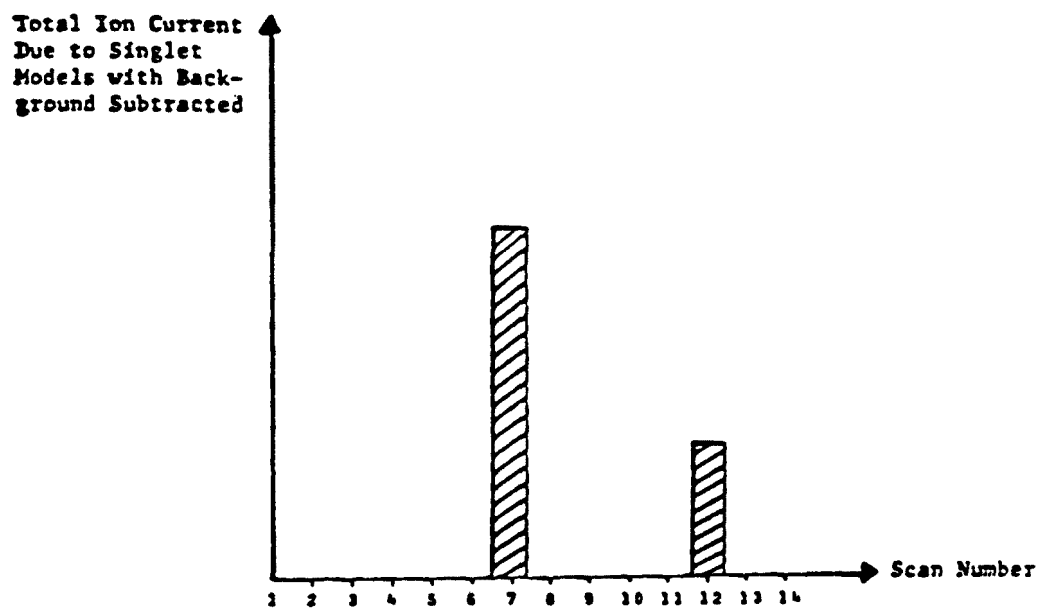
Figure 5. Statistics of TIC vs. scan number.

point in the program the "sharpness" of each candidate peak is computed. This number is a numerical approximation of the theoretical expression

$$\int \left| \frac{dy}{y} \right|$$

which is a measure of the relative steepness of each individual peak. It is to be noted that this number is independent of the height of the peak. There is a provision in the CLEANUP program for the rejection of peaks not meeting a minimum sharpness threshold (Figure 3). Noise spikes are eliminated by the property of the steepness function which favors wider peaks over very narrow ones.

Once the presence of a peak is detected, the CLEANUP program begins its real work, namely, the deconvolution of the peak mixtures and the accounting for bleed, noise, etc. The CLEANUP program assumes linear superposition of ion currents due to different causes, i.e., at any given point in time the total ion current can be represented as a simple sum of a background, column bleed, and whatever eluants are present. For the case of a singlet, the total ion current for a given mass Y(t) may be represented as a sum of three functions

$$Y(t) = P(t) + dt + c,$$

when the term dt represents the contribution to column bleed, c represents the contribution due to background noise, and P(t) is the peak contribution due to the signal. The problem lies in making an initial choice for the function P(t). The method used by CLEANUP is to examine the mass in the window with the sharpest non-saturated singlet maximum. This mass was stored by the previous phase of the program. The column bleed and background are then subtracted out (see Figure 6). Once the functional form of the model peak for a given mass is known, the contribution to the ion current due to the eluant compound at other masses can be computed via a least squares process, i.e., for any given mass

$$Y(t) \sim pP(t) + dt + c$$

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Peak Intensity

Model Peak w/background and
Column Bleed

Background & Column Bleed

Model Peak with background subtracted
to be used in Least Squares Fitting

Scan Number

1 2 3 4 5 6 7 8 9 10 11 12 13 14
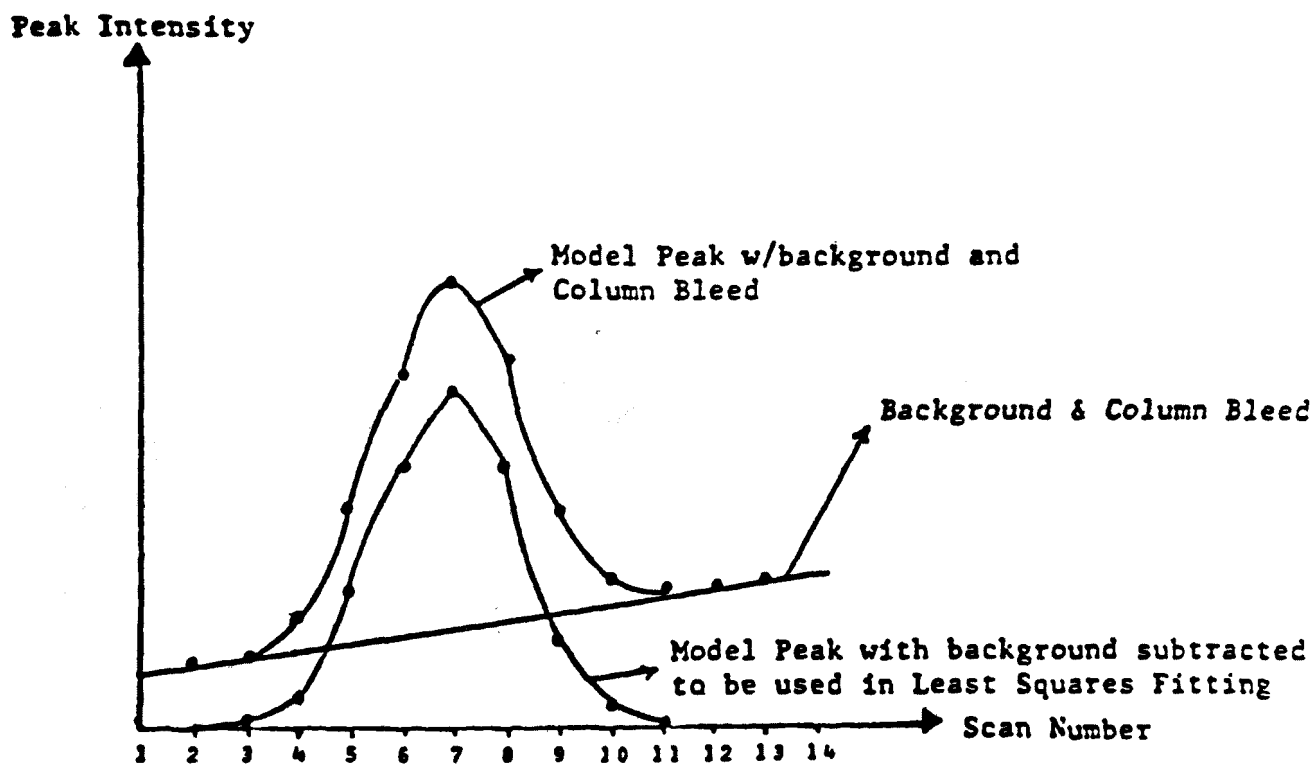
Figure 6. Example of background subtraction for model peak.

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Here Y(t) is the total signal for that mass, which is made up of a contribution of the signal, column bleed, and background. The aim is to minimize

$$D = [Y(t_i) - pP(t_i) - dt_i - c]^2$$

in the interval covered by the peak, subject to the conditions

$$\frac{\delta D}{\delta p} = 0; \quad \frac{\delta D}{\delta d} = 0; \quad \frac{\delta D}{\delta c} = 0$$

This is done by a standard method.[5] It is important to realize that p, d and c are being varied in order to find the best possible match of three functions of fixed form (the model function P, a line through the origin, and a constant) to the given Function Y. The idea is that for a given eluant, all peaks will have the same functional form P(t) and that peaks of different masses corresponding to that eluant differ only in relative amplitude - something which is taken account for in the factor p in pP(t). Once the model function P(t) is determined for a mass that is relatively free of background noise, neighboring eluents, column bleed, etc., a meaningful interpolation can be made for those masses which are contaminated with noise and bleed, or which are saturated. In the case of saturated peaks, a routine is used which interpolates an approximation of the functional form of P(t) to obtain correct signal contributions for saturated points based on the non-saturated points on the fringe of each peak.

For doublet resolution, the model peak for the neighboring spectrum is added to the approximating function. Y(t) is then approximately by

$$Y(t) \overset{\sim}{\sim} pP(t) + rR(t) + dt + c$$

where R(t) is the model function for the second peak and r is its corresponding parameter. The idea is graphically illustrated for several cases in Figure 7.

A diagram of the detailed subroutines of the CLEANUP program, along with a short description of these function is shown in Chart 1 and Table 1.

SCOPE AND LIMITATIONS

Some comments regarding the scope and limitations of the CLEANUP program are in order.
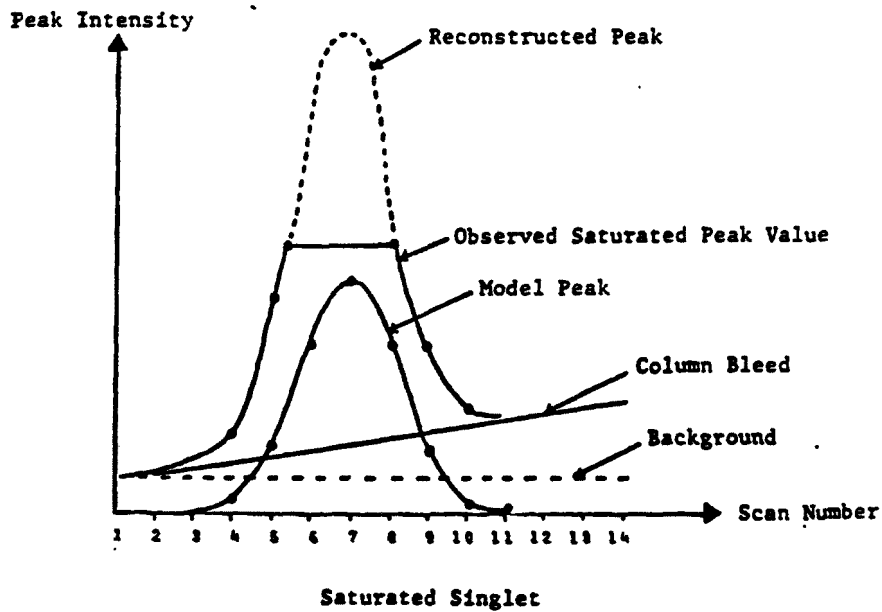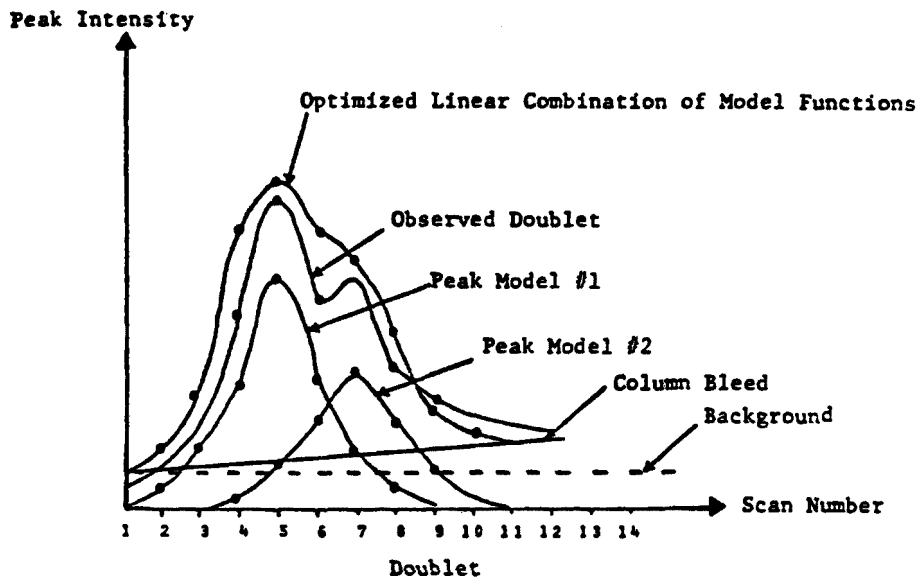
Figure 7. Peak model resolutions: two possible situations.

Inside Cleanup

MAIN$_1$

CUPRNT$_2$ TLOC$_3$ GETIIGT$_4$ OFFSET$_5$ LKAHED$_6$ OUTDAT$_7$ PARDER$_8$ SETBUG$_9$

NEWTOP$_{10}$ DETEKT$_{11}$ TLPRNT$_{12}$

NXTMAX$_{13}$ DETEKT$_{11}$ LKAPRT$_{14}$

NEWTOP$_{10}$

KAPUT$_{15}$ XTREM$_{16}$

SATLSQ$_{17}$ BACLSQ$_{18}$ TINESF$_{19}$ BLEED$_{20}$ SETGNY$_{21}$ NEWTOP$_{10}$

BLEED$_{20}$ TINESF$_{19}$ DUBLET$_{22}$
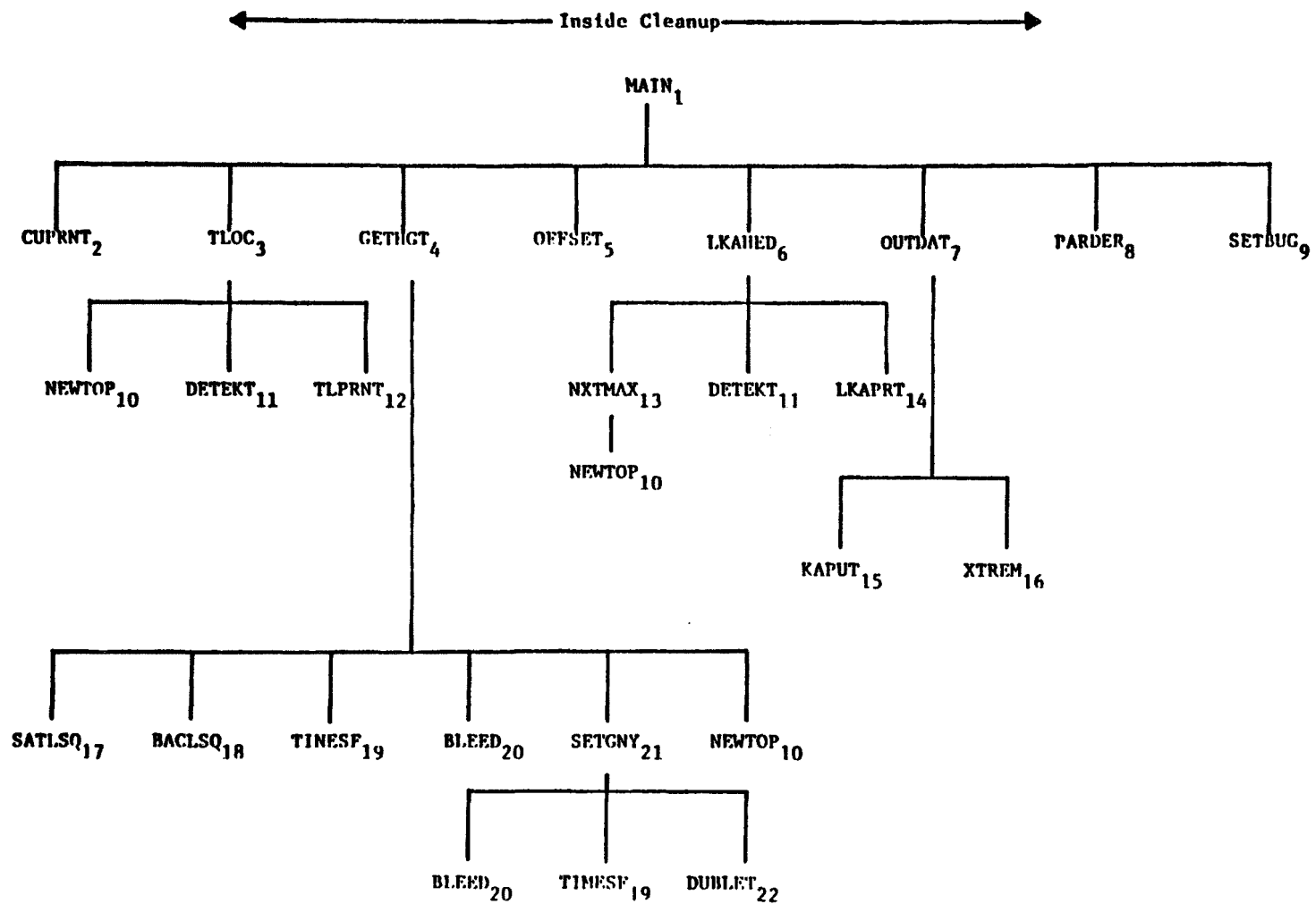
Chart 1. Summary of calling structure and subroutine function.

TABLE 1. SUBROUTINES OF CLEANUP BY FUNCTION

1. MAIN

    is the root segment which calls all other routines.

2. CUPRNT

    prints some debugging messages for MAIN.

3. TLOC

    builds histograms for eluant detection, and selects the model peak for each compound. A model peak is the singlet which is sharpest, and its mass fragmentogram is 9 spectra wide. It is important to note that histograms contain "singlet" information, and we use this information to detect eluants.

4. GETHGT

    is called after a spectrum has been detected, and is the executive for building the cleaned up spectrum from the raw data.

5. OFFSET

    is called only in the event that an overlapping situation arises, and aligns the model peaks with respect to their modes in arrays GMN and HNU in anticipation of processing a doublet.

6. LKAHED

    is called only if an eluant is detected. It looks ahead to see if another is present in the 14 spectrum window, and if so assigns the model peak and sets the flag OVLAP.

7. OUTDAT

    prints report information for the run and writes the clean up spectra to disk.

8. PARDIR

    is the operator communication subroutine. It sets some parameters which can be entered either from cards or from a terminal.

9. SETBUG

    does some initialization of output buffers, and reads in the first 13 spectra.

10. NEWTOP

    finds the actual mode and the displacement of this mode from the assumed mode as well as computing the integral $|dy|/y$ (rate) from a singlet peak profile.

(continued)

TABLE 1 (continued)

11. DETEKT

examines histograms to determine if an eluant is present.
The major criterion for an eluant to be detected is that its
histogrammed total ion current be greater than MINTIC.

12. TLPRNT

prints some debugging messages for TLOC.

13. NXTMAX

builds histograms in the look ahead mode. Due to core limi-
tations, it can only look ahead 3 spectra, and in the extreme
case, i.e., the 3rd spectrum ahead is determined to be an
eluant, the determination is done with less information than
its predecessors. If 16 spectra are in core, NXTMAX can
easily be set up to use exactly the same criteria as TLOC in
building histograms. Some heuristics have been put in TLOC
and DETEKT to take care of the minimal cases. This minimal
situation occurs when a very weak eluant is found ahead, and
then passed up when it becomes a primary candidate.

14. LKAPRT

prints some debugging message for LKAHED.

15. KAPUT

outputs to the line printer a short summary of the results of
the programs processing.

16. XTREM

determines the minimum value and its subscript given an integer
array and its length.

17. SATLSQ

processes saturated peaks, and tries to compute actual peak
heights by taking the ratios of nonsaturated amplitudes in the
saturated peak profile with their corresponding amplitudes in
the model peak.

18. BACLSQ

does a least squares fit using the peak profile of a singlet,
and a model peak to determine the singlets contribution to a
detected spectrum.

19. TIMESF

uses a parabolic interpolation to place a peak profile on the
same time co-ordinate as the model peak for a detected elutant.

20. BLEED

fits a line to a peak profile and uses goodness of fit, and
average value of Y, where Y=mx+b, to see if the profile is
column bleed.

(continued)

TABLE 1 (continued)

21. SETGHY

    is called only in the event of a doublet situation, and
    decides whether or not a given peak profile will be passed
    through the doublet resolver.

22. DUBLET

    is the doublet resolver, and does the least square fit of two
    model peaks, and a doublet peak profile and puts the second
    peak contribution in a different array.

The construction of model peaks for an eluant depends on at least one mass in the processing window having a well defined, well resolved singlet. This requirement will not be satisfied if two eluants are within roughly one scan time of each other, or if there is an unsaturated peak for use as a model, i.e. in extremely bad run conditions.

Also the CLEANUP procedure breaks down in the case of interacting elutents because the ion currents are not longer a simple sum. This is an inherent limitation of the linear reconstruction model.

Finally, the program currently lacks the capability of providing the user with a visual TIC plot. This is essential in order to allow the user to analyze the final results.

SECTION 4

IMPLEMENTATION AND TESTING OF CLEANUP

Phase II of the contract consisted of implementing a version of the Rindfleisch program on the TUCC 370 and testing its performance. This involved obtaining an existing copy of CLEANUP and modifying it to run at TUCC, developing support software to facilitate the analysis of CLEANUP output, and extensive testing of CLEANUP on a variety of environmental samples.

INITIAL PROGRAM MANIPULATION

The first step in implementation of the CLEANUP program was to obtain a listing and initial documentation from the author. This was achieved with relatively little difficulty. Dr. Rindfleisch and his colleagues were very generous in providing us with full listings and some documentation of their program. Since these programs were designed to run on a PDP-11 computer, they were written in a combination of PDP-11 assembler language and a PDP-11 version of Fortran, which would have made their translation into standard Fortran a very difficult task. We were informed by the Stanford group, however, that another group of chemists at the NASA Ames Air Force Base had been working on a Fortran implementation of the Rindfleisch program and we were referred to that group.

The Ames scientists were cooperative in forwarding their versions of the Rindfleisch programs to us, however it was immediately clear when we received tapes from them that there were large discrepancies between their programs and a working system. There were numerous errors in the program, indicating that they had not been fully tested.

After some additional conversations with the Ames group, an improved version of their Rindfleisch program was sent to us which we began to use. The new program had been chnaged, and some of the errors, detected previously had been corrected. This new program was then reorganized to make it operational in the TUCC environment. The mode of inserting variable data and

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options into the program was completely altered. The original programs were designed to operate interactively from a terminal, and the variables for each run were introduced in a conversational mode. If the results are not satisfactory, then the parameters are changed and the program re-run, etc. This process is continued until the operator is satisfied with the results, or feels that no further improvements can be made. Since in our environment programs must be run in a batch process, it was necessary to proceed somewhat differently. A set of trial parameters were obtained from the program authors, which were entered into the RTI program from cards. The effect of the program paramters on the output is discussed in 3.4.

The main body of the program was debugged by the use of the WATFIV compiler. This compiler is useful, not only because of its very well documented error messages, but because the compiler, by its nature, cannot operate using special system subroutines. This means that the entire program, if run under WATFIV, is insured to be compatible with other computers running with standard Fortran packages. By this procedure, the entire program was debugged and freed from a number of errors, particularly those relating to the initialization of variables prior to their use, which in our experience, has proven very difficult to trace down at later stages of program development.

SUPPORT SOFTWARE FOR CLEANUP

After the program ran freely, it was necessary to test it on some typical environmental data. In order to do this, GC/MS data which previously had been generated from environmental samples in the RTI laboratory were adapted to the CLEANUP program. This required the writing of several sets of programs: one translated raw mass spectral data into the input format required by CLEANUP; a second translated the output data from CLEANUP into a format required by the search program; a third set generated plot output from CLEANUP on an in-house VERSATEC plotter. A more detailed description of this software follows.

RTI Search System Interfacing

These programs accepted mass spectral data, which had been acquired on a Varian CH-7 mass spectrometer, and automatically selected spectra for introduction into a library search program. Selection of specific spectra was carried

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out by the analysis of the total ion current (TIC) profile of the GC run. In the case of spectra acquired using the Varian system, the TIC profile was very easy to analyze numerically, because the data system was designed to acquire TIC information simultaneously with MS information throughout the course of the run. By means of a multiplexer, the data system acquired ca. 100 TIC points, which were received from an ion current electrode placed at the exit of the source of the spectrometer, during each MS scan. These TIC points were recorded on the output tape in a Varian coded format and it was possible to regenerate this TIC information in both numeric and graphic form from the original tape.

Whereas most other GC/MS computer systems generate TIC data by the summation of ion intensities for each mass spectrum run (software TIC), the hardware TIC data is much richer in detail since it produces ca. 100 points per GC scan rather than one in the software method. This advantage is particularly important when data are being scanned relatively slowly as compared with the TIC peak width. The TIC trace generated from the data encoded on the tape was very useful to evaluate the CLEANUP program, since CLEANUP does not produce any visual record of the GC run, but simply selects specific peaks for subsequent evaluation, in our case by means of library search. We compared the selection of spectra made by analysis of the hardware TIC trace with those spectra chosen by CLEANUP. This approach was extremely useful in the evaluation of the CLEANUP program. Figure 8 shows a schematic diagram of the RTI data processing system.

Splicing the CLEANUP program into te RTI data processing system consisted of two parts: formatting the data generated by the MS-7 GC/MS system so that it could be read as input by CLEANUP (Chart 2) and formatting the output generated by CLEANUP so that it could be used as input to the RTI library search program (Chart 3).

As these programs were being written, a tape was prepared of a standard GC/MS run on the RTI MS-7 GC/MS system and was hand carried to TUCC. After a few trials, we were successful in creating CLEANUP-compatible input data, getting CLEANUP to run to completion on that data, and finally obtaining a successful run on that data with the RTI search program.
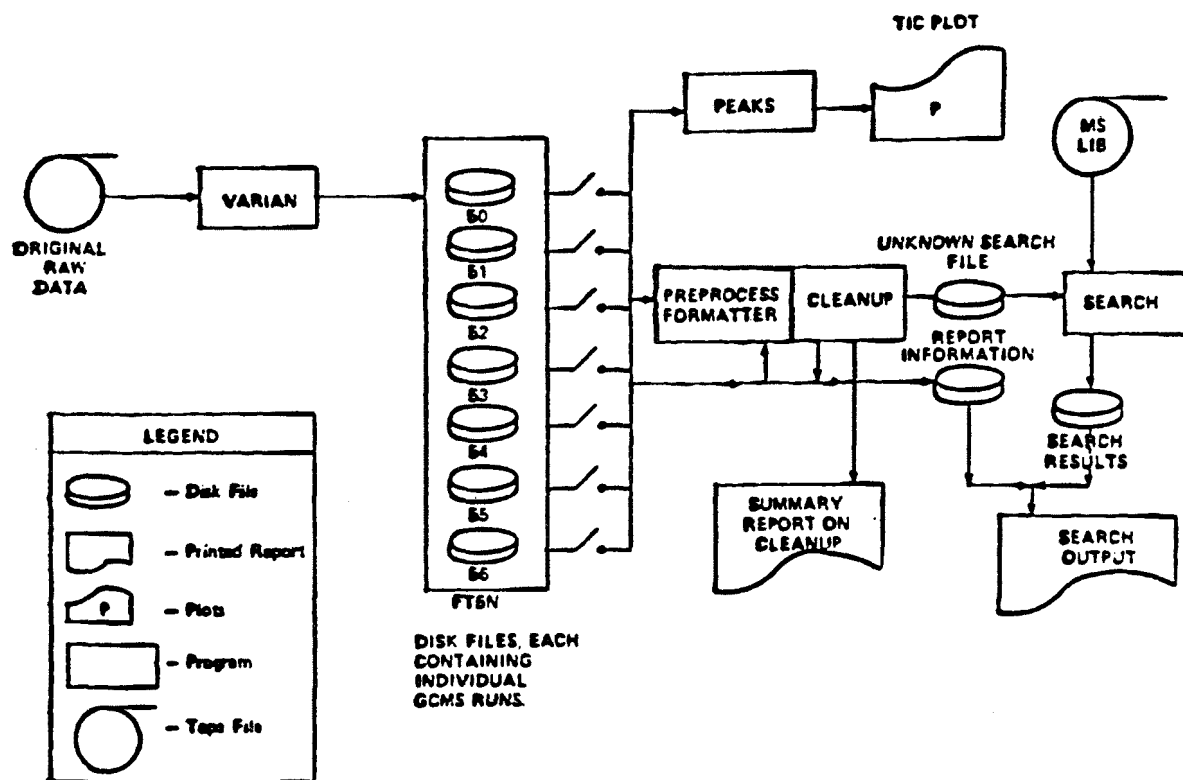
Figure 8. Overall schematic of computer assisted qualitative analysis of GC/MS data.

Varian data tape containing
raw output from GC/MS

Translates raw Varian data to
Fortran compatible format

Raw Tape File

VARIAN Pgm.

Intermediate step, output
file from VARIAN

VARIAN Disk File

VARTRN Pgm.

VARTRN is an intermediate program
which transforms the output of
VARTRN into CLEANUP compatable
input

Output file of VARTRN in
CLEANUP compatable input
format

CLEANUP Input File

CLEANUP is the main processing
program which:
  (1) Eliminates column bleed
      and background
  (2) Reconstructs saturated peaks
  (3) Resolves mixed doublets

CLEANUP Pgm.

Output file of CLEANUP
containing resolved spectra

CLEANUP Resolved Output

Chart 4:
Display of input and output
spectra on VERSATEC plotter

Chart 3:
Examination of results when
fed into RTI Search System
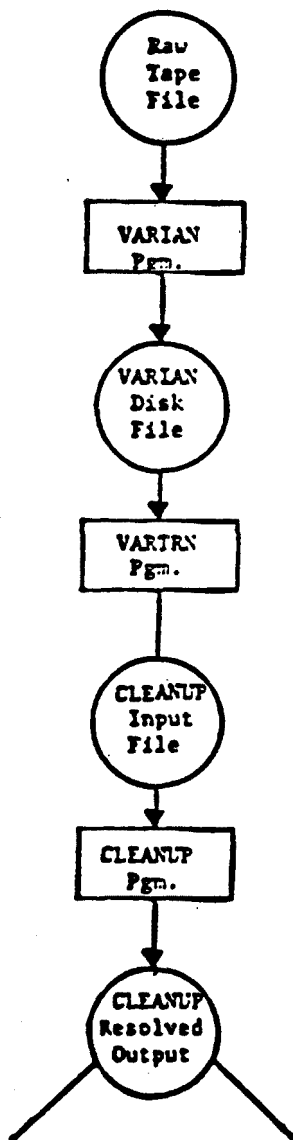
Chart 2. Steps involved in processing of CLEANUP test data (1).
Preparation for and interface to CLEANUP program.

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Input and Output
files for CLEANUP
(chart 1)

CLEANUP
INPUT

CLEANUP
OUTPUT

Sets in tens
levels of
unknowns into
appropriate
octill bracket

LEVEL
SETTING
INFORMA-
TION

SRCHTRN
PGM.

SRCHTRN converts the
output spectra from
CLEANUP into SEARCH
compatible format

SEARCH
PGM
UNKNOWN
INPUT

SEARCH searches through
a library (for each
unknown) and saves the
best fits

Search library
containing some
26,000 compounds

SEARCH
PGM
LIBRARY

SEARCH
PGM

Output of SEARCH used
by report generator

SEARCH
PGM
BEST
FITS

File of library
compound names
which are looked
up to generate
report

LIBRARY
OF
COMPOUND
NAMES

REPORT
GENERATOR

REPORT generates a
"chemists printout" of
the results from search

PRINTOUT
OF
BEST MACHINES

"Chemists Printout" of best choices for unknowns

Chart 3. Steps involved in processing of CLEANUP test data (2).
Preparation for and interface to search program.

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Plot Out for CLEANUP

At this stage it was necessary to carry out a critical evaluation of the results to determine the efficacy of the CLEANUP algorithm. Although the CLEANUP program executed successfully, preliminary examination of the printed data for a few isolated cases indicated that the initial parameters chosen were not ideal, and that although the program seemed to recognize the presence of individual components in the GC run, the output spectra were not yet suitable for characterization of the unknown GC component. In order to proceed in an orderly manner, then, it was felt that a method for displaying the results of CLEANUP needed to be developed. Software to generate plots from MS data have been available for some time, however, these programs generate output intended for the university operated CALCOMP plotters which were entirely too slow to generate the hundreds of plots needed in the course of this investigation. An alternative approach of writing software to generate plots on an in-house VERSATEC electrostatic plotter (several orders of magnitude faster than the CALCOMP incremental plotters) was adopted. The process consisted of two steps. First a program at TUCC read the CLEANUP output spectra as input and generated picture records which were then written to tape. The tape was then hand carried to the RTI laboratory and read by a PDP-12 program which generated the actual plots. This method proved very economical, since plots were generated at low costs (50¢ per picture) and high speeds (ca. 20/30 sec/plot). In this fashion it was possible to generate up to 100 plots in an hour, a task which would have tied up the TUCC network CALCOMP plotters for several days. The entire scheme for generating plots together with already existing software is shown in Chart 4 with sample output in Figures 9-11.

TEST RUNS WITH CLEANUP

Brominated Standards

A preliminary evaluation of the CLEANUP program using two GC/MS runs was made. The first was a relatively simple mixture of a series of

Input and Output
spectra files used
by CLEANUP Pgm.

CLEANUP INPUT FILE

CLEANUP RESOLVED OUTPUT

Comparison spectra after
completion of the CLEANUP
Procedure

BBPLOT is an intermediate
program which generates card
image input for a plot
generation program

BBPLOT

Disk file consisting of
card images. These control
cards contain masses and
intensities for plotting

CARD IMAGE CONTROL DATA

PLOTGEN

Existing program to
produce CALCOMP plots

Disk file consisting of a
series of pen locations which
as a group, create a plotter
picture

CALCOMP PLOT INPUT

VERPLOT PGM.

VERPLOT is a post pro-
cessor for the TUCC plotter
routines which translates
CALCOMP compatable input
plot records into VERSATEC
compatable plot records

Television screenlike series
of "black and white" bits to
be intrepreted by the Versatec.
This data set S on tape

VERSATEC PLOT INPUT

Actual paperplot output of
spectra in VERSATEC:

PLOT OUTPUT OF CLEANUP

PDP-12 VERSATEC PLOT PGM.

This program reads the
VERSATEC plotter input on
the inhouse tape drive and
generates the actual plots
on the VERSATEC.

Chart 4. Steps involved in processing of CLEANUP test data (3).
Generation of Versatec MS plots from CLEANUP files.

30
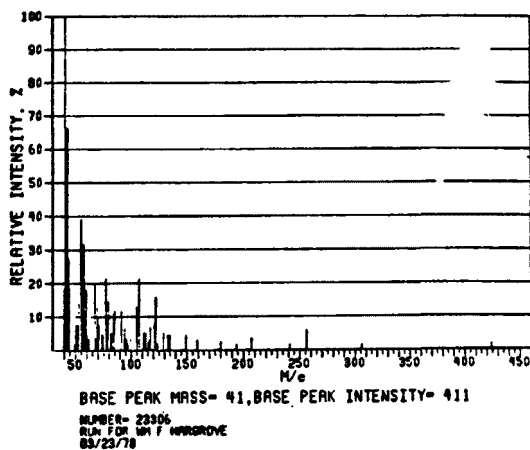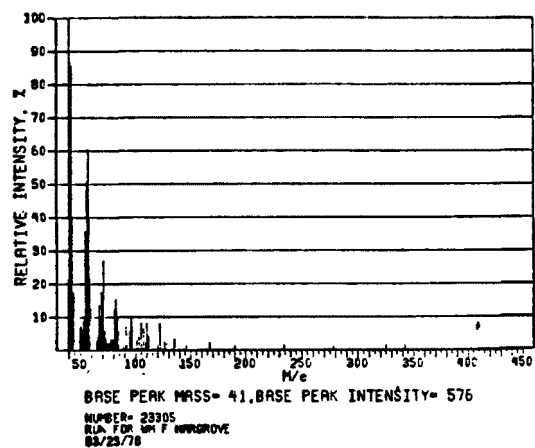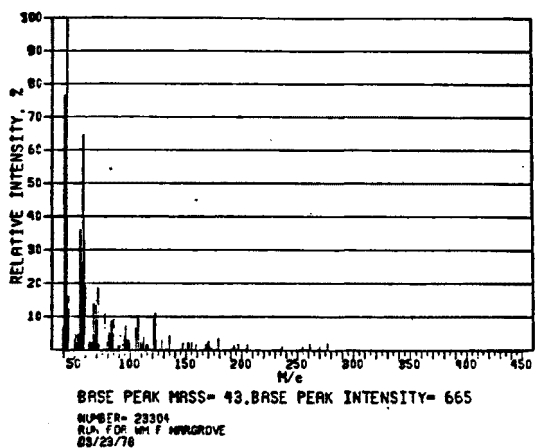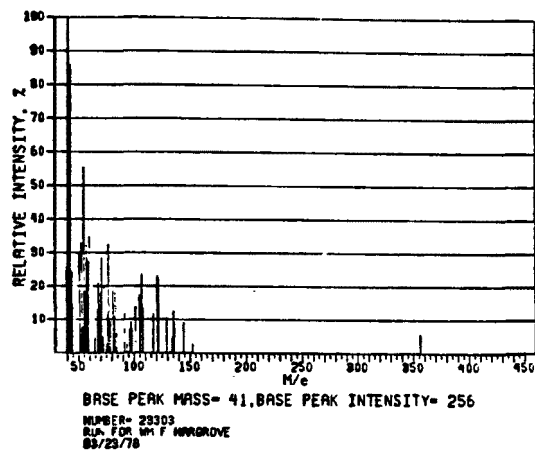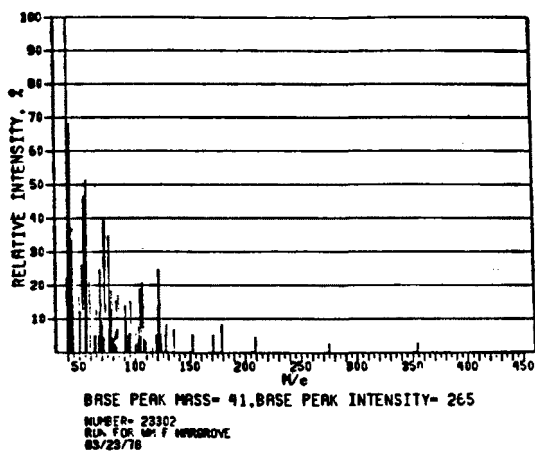
Figure 9. Five "raw" spectra used as input to CLEANUP.

BASE PEAK MASS= 43,BASE PEAK INTENSITY= 430

NUMBER= 23304
RUN FOR WM F HARGROVE
01/11/78.
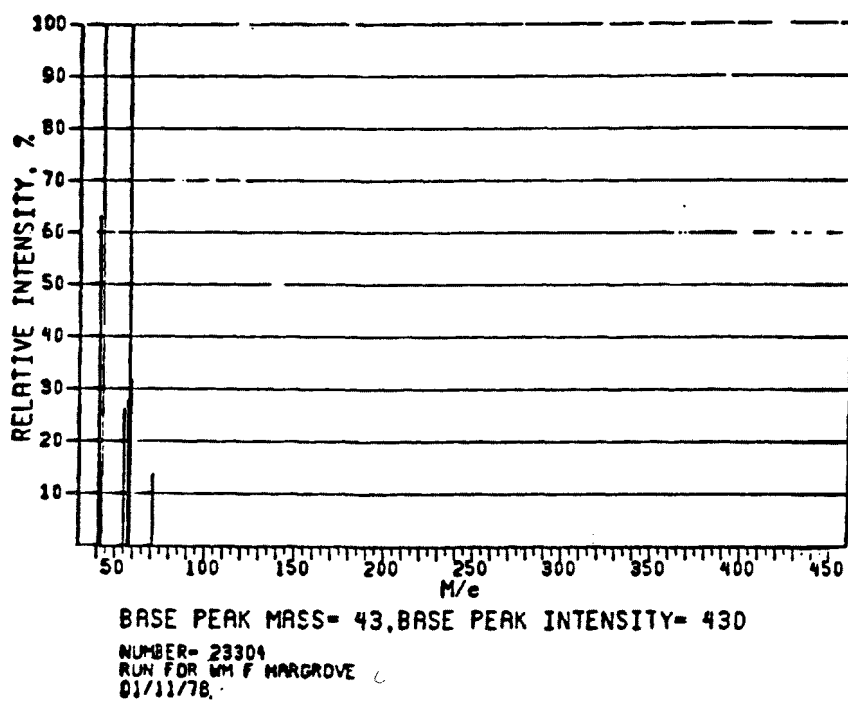
Figure 10. Resultant "cleaned-up" spectrum from Figure 9.

A

BASE PEAK MASS=149,BASE PEAK INTENSITY= 3141

NUMBER= 23452
RUN FOR WM F HARGROVE
03/23/78

B

BASE PEAK MASS=149,BASE PEAK INTENSITY= 3043

NUMBER= 23452
RUN FOR WM F HARGROVE
01/11/78
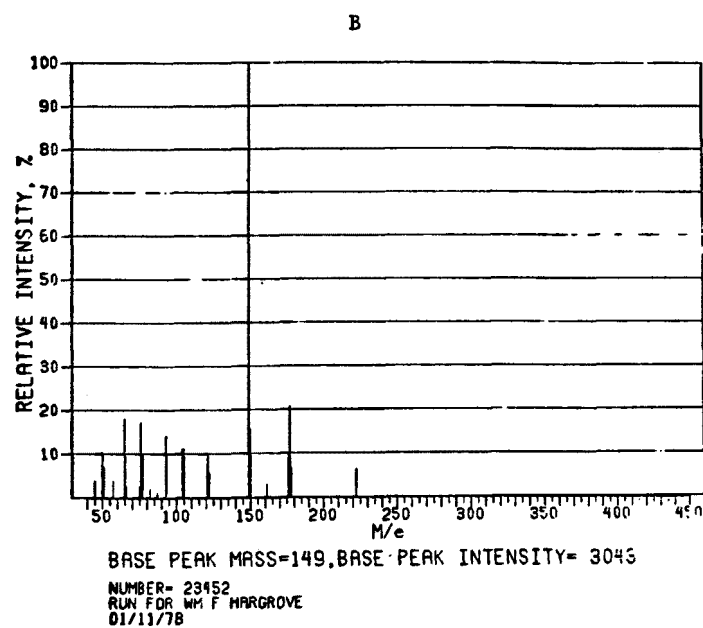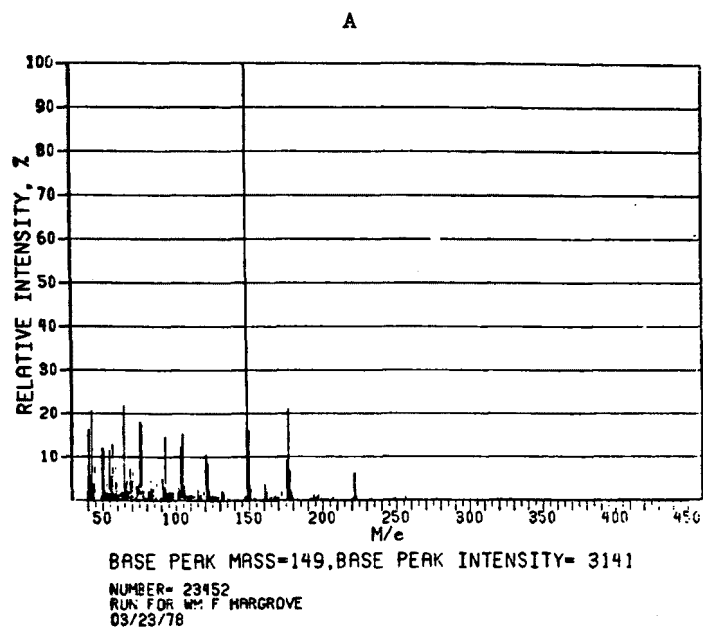
Figure 11. Precleanup - A, postcleanup - B.

brominated standard compounds. This series was chosen to serve as a control. The compounds in the run were known, and they were reasonably easy to identify.

In the case of the brominated standards, the CLEANUP procedure worked essentially perfectly. In the first section of the GC run the spectra were relatively free of background noise and the output spectra from the CLEANUP program resembled the original spectra very closely. This fact is not trivial in that it shows the CLEANUP procedure is essentially benign for the case of uncomplicated spectral data. Thus, if the original data are good, then the CLEANUP step does not alter them or degrade them in any way. This is a necessary condition of performance for a good CLEANUP program.

In the latter portions of the run, increasing amounts of background noise from column bleed became evident. In the case of weak spectra near the end of the run, the CLEANUP procedure became indispensible for the identification of several components. As it turned out, in addition to the brominated standards which were specifically put into the mixture, several additional components, many of them not containing bromine, were found. For example, spectrum number 23469 in the run had been seen many times previously during manual identification and never been identified. With the help of CLEANUP and SEARCH it was possible to identify this component as an alkylated phenol. The TIC trace of the run is given in Figure 12.

The results from the CLEANUP program are shown graphically in Figures 9 through 11. Figure 9 shows five successive spectra (the computer actually uses 7) from which a cleaned up spectrum is derived (Figure 10). Another pair of pre and postCLEANUP spectra are shown in Figure 11. A summary of the run is shown in Table 2.

Coal Run

The second GC/MS data set which was examined consisted of a low boiling fraction from a coal gasification process. With this data the situation was virtually the opposite from the previous case, i.e.,

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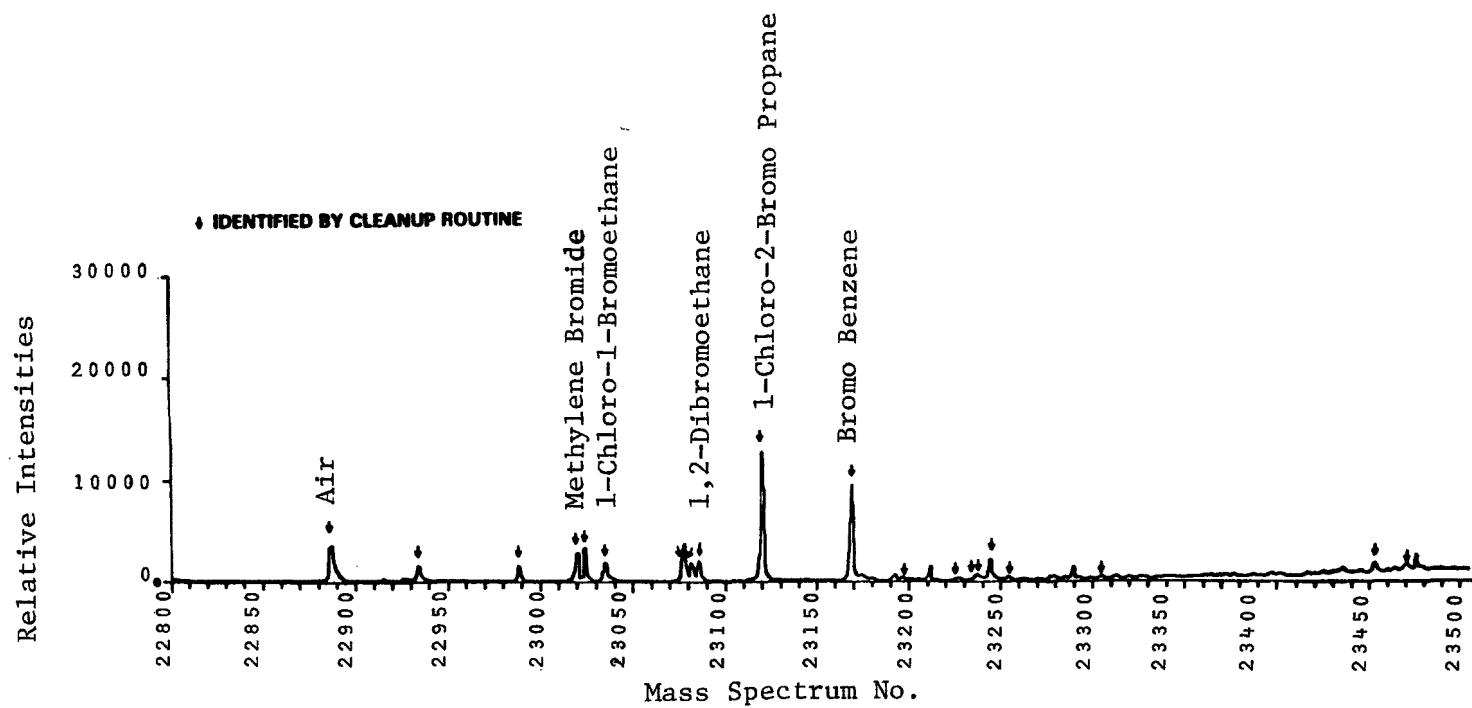
Figure 12. TIC plot of brominated standards.

Table 2.   RESULTS OF COMPARISON OF CLEANUP WITH BROMINATED STANDARDS SEARCHED FOR 26,209 STANDARDS

| | Compound | Precleanup | | | Postcleanup | | Elution |
		Rank[b]	R	TIC Max.	Rank	R	Time
1.	methylene chloride[a]	1	.31	752	1	.67	15.63
2.	1,2-dichloroethane[a]	1	.33	672	1	.54	21.93
3.	methylene bromide	1	.36	720	1	.49	25.55
4.	bromodichloromethane	1	.37	688	1	.43	26.00
5.	1-chloro-2-bromoethane	1	.30	704	1	.43	27.30
6.	n-butyl bromide	>5	<.19	512	2	.33	32.43
7.	ethylene bromide	3	.17	800	1	.31	33.25
8.	chlorobromopropane[a]	1	.28	1392	1	.37	37.22
9.	bromobenzene	>5	<.18	1088	2	.27	42.93
10.	dimethylphenol[a]	1	.31	320	1	.45	46.20
11.	n-butane[a]	>5	<.19	304	1	.53	49.35
12.	acetophenone[a]	>5	<.22	320	1	.39	51.10
13.	toluene[a]	>5	<.21	304	1	.60	52.97
14.	diethyl phthalate[a]	1	.33	478	1	.52	76.07
15.	octyl phenol[a]	>5	<.15	432	1	.52	78.05

[a] Compound was not knowingly part of standard mixture.

[b] The ordinal number of the similarity of the library component to the unknown. The program normally prints out the 5 best fits.

this sample consisted of a deliberately chosen, highly complex mixture, which would test the system to its limit to determine the most that could be expected from this program.

In this GC/MS data set, the chromatography conditions and the relatively slow sampling rate assured that the majority of MS scans would consist of mixtures, contain also background noise, column bleed, and other components in the system. Although the specific components in the mixture were not known, the nature of the sample gave strong clues as to what kinds of compounds were to be expected. A TIC plot of this run is shown in Figure 13.

Not surprisingly then, when raw coal run MS data were introduced into the MS search routines, the output was nearly totally useless, since the correlation coefficients were almost uniformly low and those compounds which were chosen as the closest fitting were obviously completely erroneous. We believe that we understand why this occurred. When samples are highly impure, numerous additional small peaks, particularly in the high molecular weight regions usually appear. The search system normally has no way of distinguishing these weak noise peaks from similar weak peaks which may be present in high molecular weight components. As a result, these peaks are picked up as possible molecular ions for high molecular weight components, and the results are entirely erroneous.

After the CLEANUP program had been applied to this set of data, the results, although far from perfect, improved noticeably. A sample of the search program output is shown in Table 3. Most of the high molecular weight noise was removed by CLEANUP, resulting in the identified compounds being of a much more "reasonable" nature. In addition, the search program's correlation coefficients rose dramatically, and indeed, most of the identified components seemed to be reasonable, based on the known origin of the sample. Thus hydrocarbons, low molecular weight phenols, and specific compounds containing heteroatoms such as thiophene and carbon disulfide were identified correctly by the search system with good correlation coefficients. We feel that this represents a remarkable achievement for such a difficult mixture. Figures 14 and 15 show a
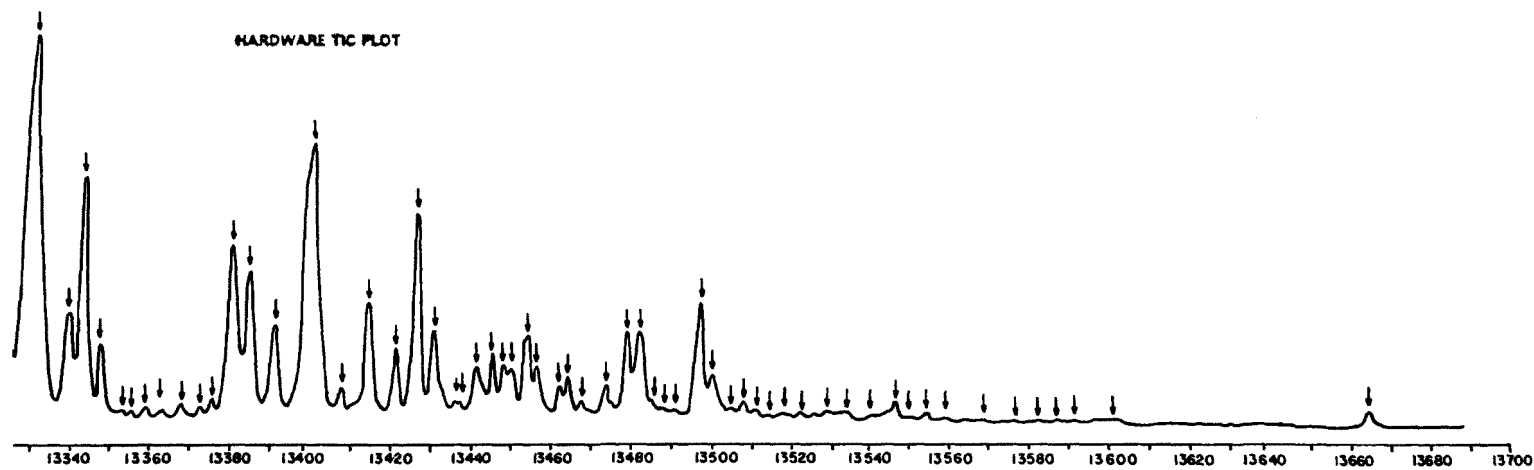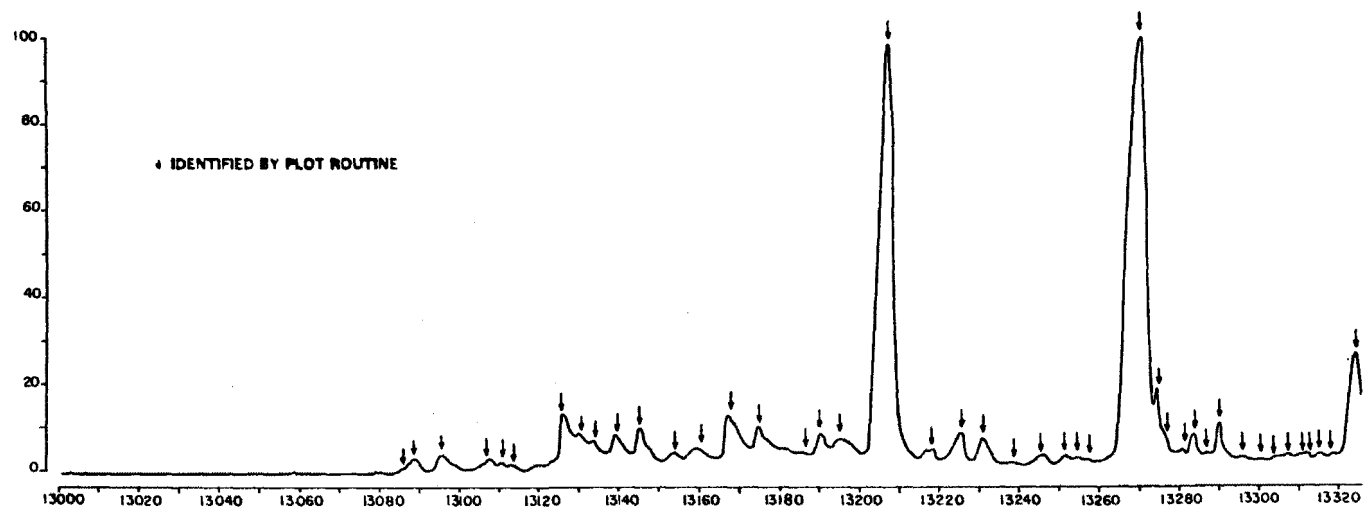
Figure 13. Hardware TIC plot of GC/MS analysis of organics from coal pyrolysis.
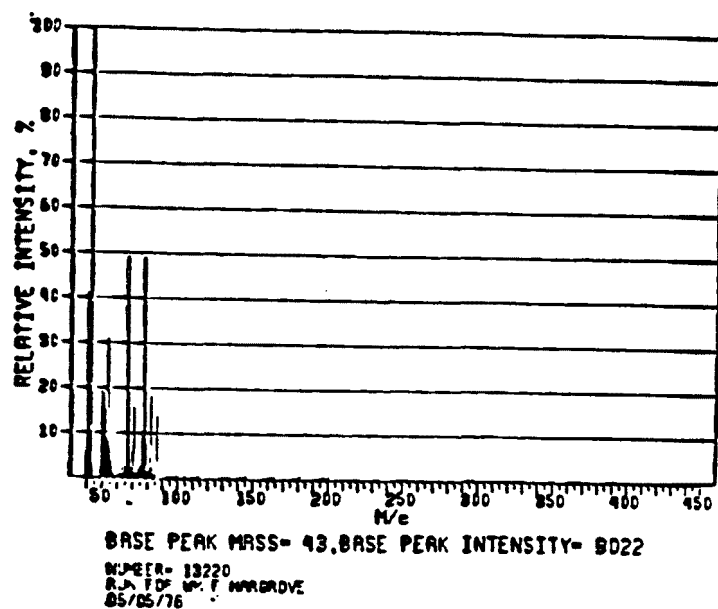
Figure 14. Typical precleanup of mass spectrum.
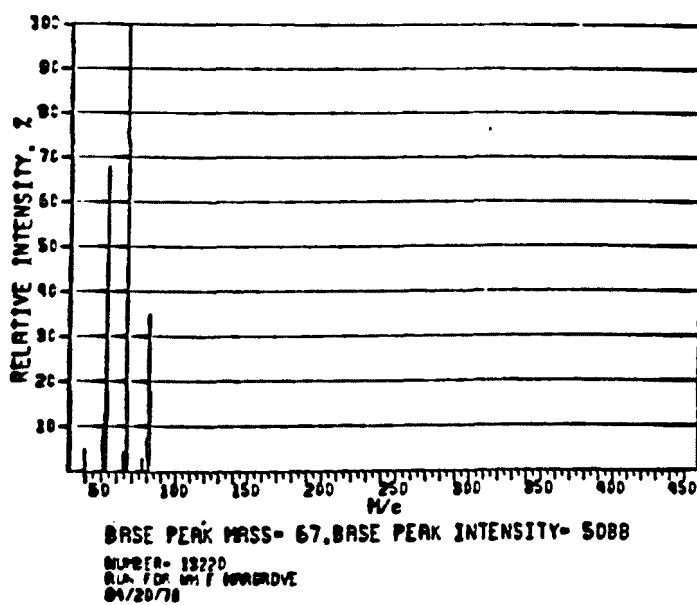
Figure 15. Same spectrum after CLEANUP.

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TABLE 3. TYPICAL PRINTOUT FOR IDENTIFICATION OF COAL COMPONENTS (AFTER CLEANUP)

SPEC # 4211   ELUTION TIME=   24.62 MIN   ELUTION TEMP=   0   TIC MAX=   928

	ID#	R	MWT	FORMULA	NAME
1.	622	0.47	88	C 4 H 8 O 2	ETHYL ACETATE
2.	2234	0.38	118	C 6 H 14 O 2	1-ISOPROPOXY-2-PROPANOL
3.	2210	0.37	118	C 5 H 10 O 3	2-METHOXYETHYL ACETATE
4.	649	0.34	88	C 5 H 12 O 1	ETHYL ISOPROPYL ETHER
5.	615	0.33	88	C 4 H 8 O 2	BUTANOIC ACID (BUTYRIC ACID)

SPEC # 4221   ELUTION TIME=   25.78 MIN   ELUTION TEMP=   0   TIC MAX=   848

	ID#	R	MWT	FORMULA	NAME
1.	14543	0.59	236	C 7 F 8	TRIFLUOROMETHYL-PENTAFLUOROBENZENE
2.	9749	0.35	186	C 6 F 6	HEXAFLUOROBENZENE
3.	14540	0.35	236	C 6 F 7 P 1	PENTAFLUOROPHENYLDIFLUOROPHOSPHINE
4.	14395	0.17	234	C 6 CL 1 F 5 S 1	PENTAFLUOROBENZENE SULPHENYL CHLORIDE
5.	13839	0.17	227	C 9 H 13 N 3 O 4	2-DEOXYCYTIDINE

SPEC # 4224   ELUTION TIME=   26.13 MIN   ELUTION TEMP=   0   TIC MAX=   1568

	ID#	R	MWT	FORMULA	NAME
1.	471	0.50	84	C 6 H 12	1-HEXENE
2.	477	0.46	84	C 6 H 12	2-METHYL-1-PENTENE
3.	475	0.46	84	C 6 H 12	METHYLCYCLOPENTANE
4.	462	0.44	84	C 6 H 12	CIS-2-HEXENE
5.	483	0.44	84	C 6 H 12	TRANS-2-HEXENE

SPEC # 4241   ELUTION TIME=   28.12 MIN   ELUTION TEMP=   0   TIC MAX=   1696

	ID#	R	MWT	FORMULA	NAME
1.	354	0.69	78	C 6 H 6	2,4-HEXADIYNE
2.	353	0.68	78	C 6 H 6	1,5-HEXADIYNE
3.	352	0.68	78	C 6 H 6	1,5 HEXADIENE-3-YNE (DIVINYL ACETYLENE)
4.	351	0.68	78	C 6 H 6	BUTADIENYL ACETYLENE
5.	350	0.51	78	C 6 H 6	BENZENE

SPEC # 4247   ELUTION TIME=   28.82 MIN   ELUTION TEMP=   0   TIC MAX=   960

	ID#	R	MWT	FORMULA	NAME
1.	471	0.54	84	C 6 H 12	1-HEXENE
2.	470	0.50	84	C 6 H 12	HEXENE-2
3.	445	0.48	84	C 5 H 8 O 1	CYCLOPENTANONE
4.	453	0.48	84	C 5 H 8 O 1	2-METHYLCYCLOBUTANONE
5.	1235	0.46	102	C 6 H 14 O 1	1-HEXANOL

SPEC # 4256   ELUTION TIME=   29.87 MIN   ELUTION TEMP=   0   TIC MAX=   1136

	ID#	R	MWT	FORMULA	NAME
1.	136	0.81	64	O 2 S 1	SULFUR DIOXIDE
2.	358	0.29	80	C 1 H 4 O 2 S 1	METHANESULFINIC ACID
3.	2175	0.29	118	CL 2 O 1 S 1	THIONYL CHLORIDE
4.	6579	0.24	159	C 2 F 3 N 1 O 2 S 1	TRIFLUOROMETHANESULFINIC ACID ISOCYANATE
5.	11530	0.23	203	H 1 N 3 O 4 S 3	2H-1,3,5,2,4,6-TRITHIATRIAZIN-1,1,3,3-TETROXIDE

typical "before" and "after" pair of spectra from the coal run. Table 4 shows a comparison of a small selection of the data before and after CLEANUP. Complete accuracy is not claimed for this run, but CLEANUP improves the hit rate from nearly zero to an estimated 50%.

Several defects in the system emerged from this series of experiments. The most obvious defect involves situations in which strong peaks emerge from the column at sufficient amplitude to saturate the data acquisition system for a number of ions in several mass spectra. The most obvious case of this involves the component benzene (Figure 13, spectrum number $\underline{ca}$. 13207), which eluted from the column as a very broad band extending for about 9 spectra (at 6 sec/scan this corresponds to a 54 second peak). This component showed saturated peak intensities for five major ions at m/z 50, 51, 52, 77, and 78. As a result of this situation, the ^{13}C isotope at m/e 79 was computed to have a relative intensity of 50%. As a result, the search program subsequently misidentified the major peaks in the spectrum and the search for benzene failed. This problem was compounded because, in addition, the large amount of benzene present caused other components, mainly from the "stationary" phase in the column to coelute, giving rise to a series of small peaks at high masses which the CLEANUP program dutifully processed and included in the unknown spectrum.

The problem of saturated peaks in spectrum identification is a serious one. Notwithstanding the fact that it is obviously wrong to try to identify components from a GC run when the amounts injected saturate the data acquisition system, these components are so strong and obvious that most investigators would be highly dissatisfied if simple compounds such as benzene were misidentified by a computer software system. There are several ways to remedy this situation. Currently, compounds with saturated peaks are labelled on the output printout (Figure 16) and thus warn the investigator of a potential problem. Also, a possible remedy for future development would be to raise cutoff limits on peak intensities when saturation was encountered so as to exclude weak peaks which otherwise would be accepted for searching.

Table 3. COMPARISON OF SELECTED SPECTRA FROM COAL GASIFICATION SAMPLE
SEARCHED BEFORE AND AFTER CLEANUP

	Before CLEANUP				After CLEANUP	
MWT	NAME	R		R	NAME	MWT
	Spectrum #13209 Elution Time = 24.38 TIC Max. 8081					
218	(AK-33)Methylcyclopentadienyl Maganese Tricarbonyl	0.19	‖	0.21	Ethyl 2-Keto-2-Penylethandate	178
200	Alpha-(Bromoethyl)Benzyl Alcohol	0.16		0.20	Ethyl 2-Hydroxy-2-Phenylethandate	180
160	P-Phenylene Diisocyanate	0.15		0.20	P-Phenylene Diisocyanate	160
133	2-Methylphenyl Azide (O-Tolyl Azide)	0.15	‖	0.20	Alpha-(Bromomethyl)Benzyl Alcohol	200
	Spectrum #13219 Elution Time = 25.55 TIC Max. 654					
198	7-Methyltridecane	0.15	‖	0.43	2-pentanone	86
142	2,6-Dimethyl-3-Heptanone	0.14		0.42	Tri-Methylacetamide	101
121	3-Acetylpyridine	0.13		0.42	2-methyl-Pentanal	100
178	Ethyl 2-Keto-2-Phenylethandate	0.13	‖	0.38	N-Butanal-D-Methyloxime	101
	Spectrum #13227 Elution Time = 26.48 TIC Max. 984					
130	Trichloroethylene	0.22	‖	0.38	Trichloroethylene	130
132	1,1,1-Trifluoro-3-Chloropropane	0.16		0.23	1,1,1-Trifluoro-3-Chloropropane	132
146	N-Carbamoyl-2-Imino-1,3-Oxathiolane	0.15		0.22	1,2-Dichloro-1,2-Difluoroethylene	132
132	2-Thisdatane	0.15	‖	0.22	1,1-Dichlorodifluoroethylene	132
	Spectrum #13233 Elution Time = 27.18 TIC Max. 862					
202	1,4-Dibutoxybutane	0.16	‖	0.56	N-Heptane	100
132	1,3-Dimethoxy-2,2-Dimethylproprane	0.15		0.47	3-Methylhexane	100
162	1-(2-Butoxyethoxy)Ethanol	0.14		0.44	2,3-Dimethylpentane	100
158	2,2-Dimethyl-5-Methylene-3,7-Dioxa-Octane	0.14	‖	0.42	2-Methyl-3-Pentanone	100
	Spectrum #13248 Elution Time = 28.93 TIC Max. 559					
98	Methylcyclohexane	0.28	‖	0.75	Methylcyclohexane	98
98	Cycloheptane	0.24		0.74	Cycloheptane	98
112	1-Methyl-1-Ethylcyclopentane	0.22		0.60	Cyclohexanone	98
98	Cyclohexanone	0.22	‖	0.58	2-Methylcyclopentandne	98
	Spectrum #13254 Elution Time = 29.63 TIC Max. 514					
146	2-Thianonane	0.21	‖	0.40	2,2-Dimethylcyclobutanone	98
146	1-Octanethiol	0.19		0.37	2-Cyclohexene-1-ol	98
188	1-Undecanethiol	0.17		0.37	Cycloheptane	98
132	1-Heptanethiol (N-Heptyl) Mercaptan	0.16	‖	0.36	3-Cyclohexenol	98

CLEAN UP OF RAW DATA FILE CLEANUP TEST #1   ON 10/28/78

SLOT	SPEC.#	TCTION	TICRAT	MAX. AMP	DOUBLET?	SAT. PEAKS
1	7110	16352.	99	32699.	NC	1
2	7130	1714.	47	747.	NC	0
3	7143	39136.	99	61726.	YES	1
4	7144	16010.	33	7089.	NC	0
5	7153	1090.	13	456.	NC	0
6	7155	15939.	90	5685.	NC	0
7	7159	2206.	44	684.	NC	0
8	7165	7353.	37	767.	NC	0
9	7175	23997.	99	10775.	YES	0
10	7177	6379.	37	2954.	YES	0
11	7178	3256.	25	1906.	NC	0
12	7192	18789.	99	9435.	NC	0
13	7197	13812.	85	4184.	YES	0
14	7189	116588.	92	28657.	NC	0
15	7191	34309.	75	13336.	NC	0
16	7192	6717.	43	1687.	NC	0
17	7204	23102.	99	9807.	NC	0
18	7209	8299.	87	2605.	NC	0
19	7216	12211.	18	6535.	YES	0
20	7217	57833.	93	27078.	NC	0
21	7221	12304.	42	4179.	YES	0
22	7225	35864.	99	13092.	NC	0
23	7230	32738.	76	8797.	YES	0
24	7236	8971.	31	2252.	NC	0
25	7238	18402.	88	3776.	NC	0
26	7244	55230.	99	25520.	NC	0
27	7259	26381.	71	7812.	NC	0
28	7265	7539.	50	1209.	NC	0
29	7287	137657.	99	32699.	NC	1
30	7289	37614.	47	9796.	YES	0
31	7292	11621.	16	4320.	YES	0
32	7293	14134.	23	3074.	NC	0
33	7295	7720.	17	2132.	NC	0
34	7299	7522.	6	1751.	YES	0
35	7302	3439.	3	1280.	YES	0
36	7374	45877.	42	70393.	YES	1
37	7338	119416.	99	32699.	NC	4
38	7315	1763.	6	1171.	NC	0
39	7322	9331.	37	3156.	YES	0
40	7375	111516.	90	32699.	NC	1
41	7336	51139.	99	32699.	NC	1
42	7341	144658.	70	32699.	NC	1
43	7346	32112.	39	16745.	NC	0
44	7351	38519.	46	13943.	YES	0
45	7355	70510.	99	32699.	YES	4
46	7356	5229.	7	1266.	YES	0
47	7358	3937.	7	2368.	YES	0
48	7362	34024.	99	32699.	YES	2
49	7365	2319.	5	744.	NC	0
50	7369	3231.	9	1244.	NC	0
51	7373	8612.	21	3104.	NC	0
52	7382	8119.	14	2775.	YES	0
53	7383	40291.	63	6658.	NC	0
54	7384	27476.	32	5946.	YES	0
55	7385	30808.	25	2245.	NC	0
56	7390	177912.	55	32699.	YES	2
57	7392	194676.	78	20230.	NC	0
58	7399	73934.	30	16678.	YES	0
59	7403	34758.	26	7034.	YES	0
60	7404	5880.	4	1480.	YES	0
61	7408	6438.	5	2012.	YES	0
62	7409	4782.	4	1985.	YES	0
63	7411	9557.	7	4904.	YES	0
64	7413	9112.	9	2847.	YES	0
65	7417	44985.	34	16888.	YES	0
66	7421	288286.	97	32759.	NC	2
67	7431	161146.	53	32699.	NC	1
68	7433	122713.	99	32699.	YES	1
69	7437	67547.	38	15925.	YES	0

Figure 16. Chemist's printout from CLEANUP.

70	7439	77009.	19	5933.	NL	0
71	7445	48464.	43	15673.	YES	0
72	7447	14978.	11	4088.	YES	0
73	7448	32380.	28	7289.	NC	0
74	7453	12165.	10	1736.	NC	0
75	7458	5804.	5	1529.	YES	0
76	7459	15669.	15	3084.	YES	0
77	7463	20917.	22	6761.	NC	0
78	7468	80867.	99	32699.	YES	2
79	7469	3856.	3	1986.	YES	0
80	7471	5719.	6	1777.	YES	0
81	7472	21524.	28	3765.	NC	0
82	7478	259586.	74	32699.	NL	7
83	7482	22038.	21	3463.	YES	0
84	7483	7770.	8	1012.	YES	0
85	7484	4966.	6	713.	YES	0
86	7486	5509.	4	1393.	YES	0
87	7439	124812.	67	18205.	NC	0
88	7490	101103.	54	29322.	NC	0
89	7497	19823.	22	2731.	YES	0
90	7498	18524.	12	2777.	NC	0
91	7504	13503.	6	1924.	YES	0
92	7505	81709.	33	14600.	NC	0
93	7511	307985.	97	32699.	NC	2
94	7513	33757.	17	7284.	NC	0
95	7516	2664.	3	514.	NC	0
96	7520	48239.	42	9673.	NC	0
97	7524	65144.	57	9421.	YES	0
98	7528	18459.	27	4667.	NC	0
99	7532	4643.	7	946.	NC	0
100	7534	5306.	9	1000.	NC	0
101	7544	17751.	29	2080.	NC	0
102	7546	14371.	25	3540.	NC	0
103	7552	26178.	48	5355.	NC	0
104	7556	94184.	53	20048.	YES	0
105	7557	100720.	99	22306.	NC	0
106	7559	2218.	3	540.	NC	0
107	7562	79264.	88	15105.	NC	0
108	7564	13380.	23	3684.	NC	0
109	7569	57043.	79	13283.	YES	0
110	7571	20409.	31	4879.	YES	0
111	7573	29182.	42	6078.	YES	0
112	7577	10942.	17	3371.	NC	0
113	7588	27725.	40	6134.	YES	0
114	7590	38307.	56	9176.	NC	0
115	7596	97445.	93	22153.	NC	0
116	7602	3966.	6	1505.	NC	0
117	7606	2180.	3	1642.	NC	0
118	7615	6393.	10	1785.	NC	0
119	7619	3496.	5	1390.	YES	0
120	7623	16928.	24	2310.	NC	0
121	7629	3851.	6	771.	YES	0
122	7630	6274.	10	700.	YES	0
123	7634	74177.	56	16870.	NC	0
124	7637	3058.	4	772.	YES	0
125	7639	4655.	7	1607.	NC	0
126	7649	3291.	6	880.	NC	0
127	7659	4311.	5	1597.	YES	0
128	7660	21496.	34	8647.	NC	0
129	7672	38809.	99	32699.	NC	2
130	7674	40636.	48	15488.	YES	0
131	7675	1338.	2	1022.	NC	0
132	7696	19246.	34	6373.	NC	0
133	7703	3835.	8	1041.	NC	0
134	7705	1525.	3	615.	NC	0
135	7710	1563.	3	1278.	NC	0
136	7717	36074.	44	8402.	NC	0
137	7723	29546.	53	7979.	NC	0
138	7775	10576.	26	1758.	NC	0

Figure 16, Continued.

Analysis of Environmental Samples

As a further test of the proper operation of the CLEANUP program, a series of runs were processed at RTI using data which had been previously analyzed by hand. Seven runs were processed which represented a selection of different types of samples which possessed a variety of functional group types. These runs are briefly described in Table 5. Of all of the runs for which data were available, one represented a very complex mixture containing a wide variety of components and was chosen for extended study. The sample was that derived from ambient air in a basement of a residence which had been built over an industrial chemical dump and which had been perfused with a large variety of organic components. The air sample when analyzed by GC/MS, showed the presence of in excess of 100 components. A total ion current plot of this run is shown in Figure 17. The sample was first processed by the CLEANUP program using the best available values for the input parameters, and the results compared with the manual identification. The results of this comparison are shown in Table 6.

Notwithstanding a small number of errors, it is obvious that the CLEANUP program is operating very successfully, and is capable of extracting correct spectra from mixtures and identifying them even in very difficult and complex mixtures. The table shows a number of interesting results. It should be noted that in the majority of cases, the manual identification and the computer results were the same. When this is combined with a high correlation coefficient (R>0.6), then the identification can be said to be correct and confirmed. In such cases the table entry is marked with an H (hit).

In some cases the computer results identified a component which is known to have a spectrum very similar to the manually identified compound. The correct identity often can be deduced by inspection, e.g. toluene might be identified as a methyl hexatriyne, or vinylidine chloride confused with dichloroethylene. This category comprises mainly isomers or homologues. These cases were also marked with an H. When the computer printed the manually identified compound as a 2nd to 5th choice, this number was also included in the table under the column heading, "Found".

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TABLE 5. DESCRIPTION OF TYPES OF SAMPLES INVESTIGATED TO TEST OUT CLEANUP

All samples were run by desorption from TENAX GC cartridges.

Type of Sample	Contents
1. UNC smog chamber	esters nitrates dioxanes nitriles aldehydes hydrocarbons low m.w. alkyl aromatics ketones
2. Oil shale volatiles	nitriles alcohols sulfur compounds ketones pyridines pyrazoles quinolines hydrocarbons aromatics
3. Volatiles from in situ coal gasification (tar fraction)	alkanes alkyl aromatics very few hetero atom containing compounds
4. Volatiles from in situ coal gasification (water fraction)	alkanes sulfur compounds pyridines oxygenated hydrocarbons
5. Organics from air in basements	alkanes aromatics chlorines, bromine and fluorine containing compounds
6. Organics in air in the vicinity of a Du Pont plant	halogenated hydrocarbons aldehydes ketones phenols nitro aromatics
7. Organics near a pesticide plant	halogenated hydrocarbons sulfur compounds oxygenated hydrocarbons (aldehydes, ketones, phenols, esters)
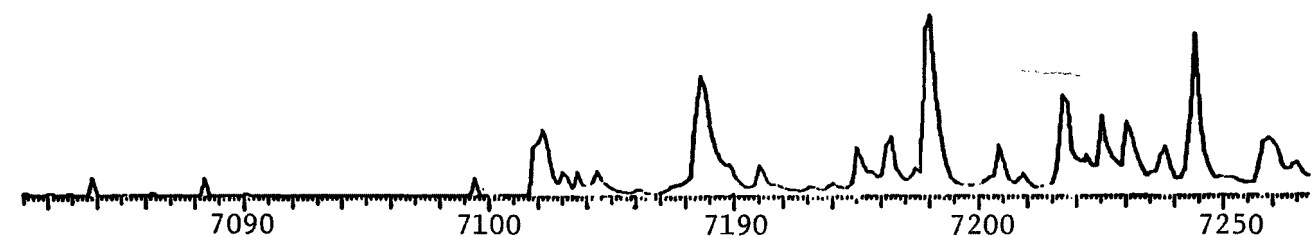
300-7849 LM 1510/CAB383N/FNYNFKA/T1/27FEB70/105MSF30   STEP SPECN. 1   INT. 1000
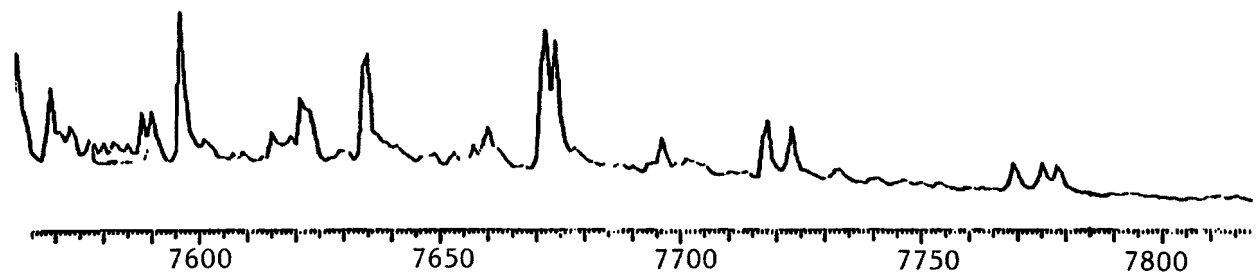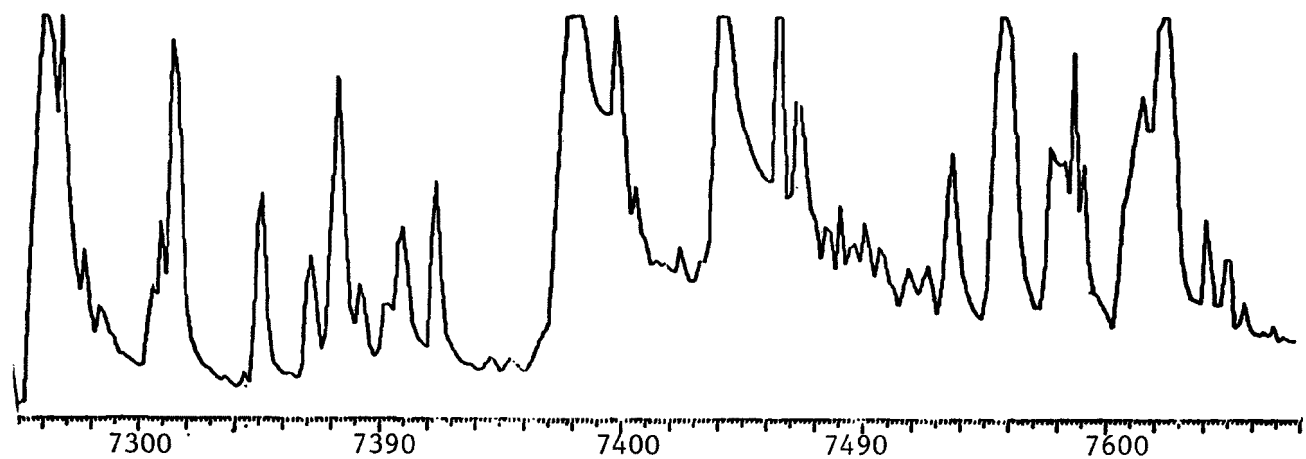
Figure 17.   Total ion current plot from test run.

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TABLE 6. COMPARISON OF MANUAL VS. COMPUTER IDENTIFICATION OF GC-MS RUN

Run #: 1510-CAB-3B3W-FNYNFKB

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7110	12.72	Dimethylamine	.84	M	5	Carbon dioxide
7130	15.05	Vinyl fluoride	.63	H		C_3H_8O?
7143	16.57	Acetone	.89	H		Acetone
7144	16.68	Fluorotrichloromethane	.85	H		--
7153	17.73	Vinylidine chloride	.78	H		Dichloroethylene
7155	17.97	Dichloromethane	.96	H		Dichloromethane
7159	18.43	Freon 113	.54	H		--
7165	19.13	Acetic acid	.71	M		C_4H_8O?
7175	20.30	2-Methylpentane	.80	H		2-Methylpentane
7177	20.55	1,2-Dimethylpropyl acetate	.55	M		C_5H_{10}
7178	20.65	n-Butanal	.75	H		Butanal
7182	21.12	2,2-Dimethylbutane	.69	H		3-methylpentane
7187	21.70	Hexafluorobenzene	.78	H		Hexafluorobenzene
7189	21.93	n-Hexane	.82	H		n-Hexane
7191	22.17	Chloroform	.63	H		Chloroform
7202	23.45	Perfluorotoluene	.71	H		Perfluorotoluene
7204	23.68	Methylcyclopentane	.77	H		Methylcyclopentane
7209	24.27	1,1,1-Trichloroethane	.68	H		1,1,1-Trichloroethane
7216	25.08	Isopropyl acetate	.76	H		Isopropyl acetate

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(continued)

TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7218	25.20	Benzene	.90	H		Benzene
7220	25.67	Acetic acid	.67	H		Acetic acid
7225	26.13	2-Methylhexane	.78	H		2-Methylhexane
7230	26.72	3-Methylhexane	.89	H		3-Methylhexane
7235	27.42	Dimethylcyclopentane	.82	H		C_9H_{14}
7238	27.65	Trichloroethylene	.75	H		Trichloroethylene
7244	28.35	n-Heptane	.97	H		n-Heptane
7259	30.10	Methyl isobutyl ketone	.54	H		4-Methyl-2-pentanone
7265	30.80	n-Heptyl formate	.76	?		C_8H_{18}
7281	32.78	1,5-Heptadien-3-yne	.60	H	5	Toluene
7289	33.60	3-methylheptane	.91	H		C_8H_{18}
7292	33.95	Hexanal	.61	H		$C_6H_{12}O?$
7293	34.07	1,3-Dimethylcyclohexane	.62	H		C_8H_{16}
7295	34.30	Ethyl n-butanoate	.52	H		--
7300	34.77	4-Methyltriazole	.46	?		C_8H_{16}
7303	35.12	n-Butyl acetate	.42	H		n-Butyl acetate
7305	35.35	3,4-Epoxy-2-hexanone	.52	M		n-Octane
7309	35.82	Tetrachloroethylene	.58	H		Tetrachloroethylene
7315	36.63	Hexamethylenecyclohexasiloxane	.57	?		--
7322	37.45	2,6-Dimethylheptane	.78	H		C_9H_{20}
7325	37.80	Chlorobenzene	.80	H		Chlorobenzene

TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7336	39.08	1,3-Dimethylbenzene	.83	H		Ethylbenzene
7342	39.67	N-Methyl-n-pentylhydrazine	.74	M	3	Xylene isomer
7346	40.25	3-Methyloctane	.81	H		C_9H_{20}
7351	40.83	Benzocyclobutane	.75	H	3	Styrene
7355	41.30	p-Xylene	.77	H	3	o-Xylene
7356	41.42	1,3-Dimethylcyclopentane	.40	?		--
7358	41.65	1-Methyl-4-ethylcyclohexane	.43	H		C_9H_{18}
7361	42.16	n-Nonane	.69	H		n-Nonane
7365	42.47	Diethyl methylvinylsilane	.51	?		--
7369	42.93	1-Methylethylcyclohexane	.75	H		C_9H_{18}
7373	43.40	Isopropylbenzene	.56	H		Isopropylbenzene
7381	44.45	Cyclohexyl acrylate	.63	?		C_3-Alkylcyclohexane
7383	44.57	3-Methylnonane	.52	H		$C_{10}H_{22}$
7384	44.68	Di(2-ethylhexyl) ether	.56	H		--
7385	44.80	2-Methyl-5-ethyl heptane	.28	H		$C_{10}H_{22}$
7390	43.38	Benzyl chloride	.58	H	2	Chlorotoluene
7392	45.62	4-Azido-3-nitrotoluene	.37	M		--
7399	46.43	Isopropylbenzene	.38	H		C_3-Alkylbenzene
7403	46.90	3-Methylnonane	.77	H		$C_{10}H_{22}$
7404	47.02	3-Phenyl-3-methylazetidine	.66	?		--
7408	47.48	p-Menthan-9-ol	.45	H	2	$C_{10}H_{20}$

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TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7409	47.60	β-Thujene	.41	H		$C_{10}H_{20}$
7412	47.83	Valeric acid	.66	H	3	Heptanoic acid?
7413	48.07	4-n-Propyl-3-heptene	.42	M		C_3-Alkylbenzene
7417	48.53	Octamethylcyclooctasiloxane	.52	?		--
7420	49.00	o-Chlorobenzoyl chloride	.43	H	2	Dichlorobenzene isomer
7431	50.17	1,3-Dichlorobenzene	.53	?		C_4-Alkylbenzene
7433	50.40	Cuminic aldehyde	.48	?		C_3-Alkylbenzene
7438	50.87	1-p-Menthadiene	.76	H		$C_{11} + C_{10}$ isomer
7439	51.10	Isobutylcyclohexane	.51	M		Bromotoluene isomer
7444	51.80	p-Methylacetophenone	.68	H	4	C_4-Alkylbenzene
7447	52.03	4-Ethylheptane	.53	H	2	$C_{11}H_{24}$ Isomer
7448	52.15	O-Decyl-hydroxylamine	.50	?		$C_{11}H_{24}$ Isomer
7453	52.73	Bicyclo(4.4.0)decane	.42	?		$C_{11}H_{24}$
7458	53.32	3,5-dimethylmethyl benzoate	.33	M		C_4-Alkylbenzene
7459	53.43	Ar,α-dimethylstyrene	.50	H		--
7463	53.90	Linalol	.39	?		$C_{11}H_{22}$
7468	54.48	n-Undecane	.87	H		n-Undecane
7469	54.60	t-Butylbenzene	.28	?		--
7471	54.83	Methyl benzoylacetylene	.36	M		Tetrachlorobenzene
7472	54.95	o,α-Dichlorotoluene	.38	H		Trichlorotoluene
7478	55.65	2,6-Dichlorotoluene	.70	H		Dichlorotoluene

(continued)

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TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7482	56.12	α-Neoisomenthol	.21	M		Pentachlorobutadiene
7484	56.23	Bicyclo(3.3.1)nonane-2-ol	.28	M		Trichlorobenzene
7485	56.35	Methyldichlorocyclopentadiene	.25	M	2	Trichlorobenzene
7486	56.58	3,4-Dimethylstyrene	.45	?		C_5-Alkylbenzene
7488	56.82	α-Pinene oxide	.77	H		$C_4H_{16}O$
7490	57.05	2,6-Dichlotoluene	.85	H		Dichlorotoluene
7497	57.87	N-Acetyl-phenylalanine	.21	M		--
7498	57.98	2-Methylnonane	.43	H		--
7504	58.68	1,2,4-Trichlorobenzene	.43	H		Trichlorobenzene
7506	58.80	1,2,4-trichlorobenzene	.48	H		Trichlorobenzene
7511	59.50	Quinoline butiodide	.43	M	3	Naphthalene
7513	59.73	n-Dodecane	.65	?		Methyl salicylate
7515	60.08	Verbenone	.33	?		$C_{12}H_{26}$
7520	60.55	1,3,5-Trichlorobenzene	.72	H		Trichlorobenzene
7525	61.02	Hexachlorobutadiene	.69	H		Hexachlorobutadiene
7528	61.48	Carvone	.74	H		?
7532	61.95	Pentobarbital-TMS ether	.20	M		Unsat. hydrocarbon
7534	62.18	Cyclohexylmethanol	.31	M		$C_{13}H_{26}$
7544	63.35	α,2,4-trichlorotoluene	.37	H		Trichlorotoluene
7546	63.58	2-Methyl-5-ethylheptane	.64	?		$C_{14}H_{28}$

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(continued)

TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7552	64.28	Bornyl formate	.59	H		$C_{10}H_{16}$(?)
7556	64.75	n- Tridecane	.67	H		n-Tridecane
7558	64.87	α,3,4-Trichlorotoluene	.67	H		Trichlorotoluene
7559	65.10	Haloperidol	.28	M		Methylnaphthalene
7561	65.45	α,3,4-Trichlorotoluene	.25	H		Trichlorotoluene
7564	65.68	1-Methylnaphthalene	.61	H		α-Methylnaphthalene
7568	66.27	Chlorophenyldibenzoazepine	.32	M		$C_{14}H_{30}$?
7571	66.50	1,2,3,4-Tetrachlorobenzene	.68	H		Tetrachlorobenzene
7573	66.73	α,2,4-Trichlorotoluene	.63	H		Trichlorotoluene
7577	67.20	2,5-Dimethylundecane	.48	H		$C_{13}H_{26}$ isomer
7588	68.48	Acenaphthene	.50	H	2	Biphenyl
7590	68.72	1,2,3,4-Tetrachlorobenzene	.68	H		Tetrachlorobenzene
7596	69.42	n-Tetradecane	.79	H		n-Tetradecane
7602	70.12	2,6-Dimethylnaphthalene	.47	H		C_2-Alkylnaphthalene
7607	70.58	2-Amino-4-hydroxupteridine	.40	M		C_2-alkylnaphthalene
7615	71.63	α-murolene	.24	M		Alkylbenzene?
7619	72.10	1-Cyclohexyloctane	.39	H	2	$C_{16}H_{32}$
7623	72.57	2,6-Di-t-butyl-1,4-benzoquinone	.61	H		C_6H_{24}O?
7624	73.27	7-Acetoxy-p-menth-1-en-3-one	.31	?		--
7630	73.38	2,6-Dichlorobenzal chloride	.32	H	2	Tetrachlorotoluene
7634	73.85	n-Pentadecane	.82	H		n-Pentadecane
7637	74.20	Methyl laurate	.38	?		$C_{15}H_{30}$

(continued)

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TABLE 6 (continued)

SP #	Retention Time	Compound Identification	R	Hit or Miss	Found	Manual Identification
7639	74.43	Trihydroxy benzoic acid, TMS	.19	M		C_3-Alkylnaphthalene
7649	75.60	Pentachlorobenzene	.38	?		C_5-Alkylbenzene
7659	76.77	Dicyclohexyl ether	.30	?		--
7660	76.88	Diethyl phthalate	.68	H		Diethyl phthalate
7672	78.28	Neopentylphosphonyldichloride	.41	M		Trimethylpentadiol diacetate
7674	78.52	n-Hexadecane	.58	H		n-Hexadecane
7675	78.63	2-Phenyldecane	.39	H		Sat. hydrocarbon
7696	81.08	Pristane	.66	H		$C_{18}H_{38}$
7703	81.90	Dimethylbenzylisobutyl ether	.23	M		$C_{16}H_{32}$
7705	82.13	Methylfuranyl THP-ether	.29	M		--
7710	82.72	Trimethylamine	.65	M		--
7718	83.53	n-Tetradecane	.77	H	3	n-Heptadecane
7723	84.23	Pristane	.82	H		$C_{19}H_{40}$
7775	90.30	Myristic acid	.48	H		?

An interesting situation occurred in a few cases in which manual identification was not possible or uncertain. In those cases the manual identification column contains a question mark. If in addition the R factor from the computer is sufficiently high, it is reasonable to assume that the computer identification is correct and the manual identification is incorrect. This is particularly true with closely spaced doublets where frequently it is nearly impossible to separate components manually. In these cases, the computer identification is more certain than the human one. When this occurred, a question mark or even an H was entered in the hit column. Components missed in the manual interpretation were marked with a dash in the appropriate column.

In a small number of cases, computer identification is undoubtedly wrong. This is usually accompanied by low R factors (R<0.3). Also when peaks are weak or small components of multiplets, it is difficult to identify them by computer. Such cases are marked with an M in the hit column ("Miss").

Comparison of figures clearly shows that the CLEANUP program materially simplifies the spectra prior to their submission to the search program. The data here presented show that by combining CLEANUP with an efficient search procedure, results can be obtained which are comparable with human interpretation. In summary, of 138 components, definite hits were obtained on 90 components, clear misses occurred in 26 cases, with 22 cases unclear. Removing the questionable category, the system recorded 78% hits and 22% misses, a rather remarkable performance for this very complex and convoluted mixture.

CLEANUP CONTROL PARAMETERS

The conclusion of Phase II consisted of variation of the CLEANUP control parameters in order to determine their effect on the output spectra and to arrive at an optimum setting for each. The fifth of the eight runs described above was chosen as a test case. Most of the parameters represent threshold settings concerned with eluant detection: peak sharpness requirements, total ion current threshold, closest expected distance between neighboring eluants, the percent of each peak attributable to background, etc. Two parameters are simply switches controlling optional diagnostic messages useful for program debugging.

An attempt was made to determine optimal parameter settings by
varying parameters in a regular manner and analyzing the results using
the SPSS statistical package. This approach was not fruitful since
there was no obvious demarcation between what constitutes reak peaks and
noise peaks, and so the statistics did not show a clear preference for
one setting of the parameters, but only a contininuum of change. Trial
and error variation of the parameters, though less sophisticated, proved
more effective. The general procedure was to vary each parameter in
both directions about the value suggested by the program authors in the
original CLEANUP documentation. A summary of conclusions and recom-
mended values is shown in Table 7. The two things which most aided
determining the effects of parameter variation were the "chemist's
summary printout" of CLEANUP (Figure 17) and the output of the RTI
search program (Table 4). It is to be emphasized that these values
represent optimum settings for a VARIAN CH-7. Our suggested values for
the INCOS test data are shown in Figure 27.

The chemist's printout is a summary list of components found by
CLEANUP, along with information regarding the presence of doublets and
saturated peaks. By comparing the change of the number of eluants
indicated in the chemist's printout together with the most likely candi-
dates for those eluants found by the RTI search program, it was possible
to determine when erroneous peaks were beginning to be picked up by
CLEANUP.

Following is a technical review of the analysis of parameters,
primarily of interest to programming specialists.

The first two variables control the print options of the CLEANUP
program and do not affect any internal calculations. Either variables
can be set to 0 (do not print) or 1 (print). The first option (IPFLAG)
determines whether or not the chemist's printout is to be printed. The
listing of all eluants found by CLEANUP takes relatively little space,
and has proved helpful in almost all test runs. We feel that the chemist's
printout should always be requested. The second option (IDEBUG) deter-
mines whether or not intermediate calculations and decisions inside
CLEANUP are to be printed. Information printed includes histogram

TABLE 7. CLEANUP INPUT PARAMETER SUMMARY

Name	Function	Possible values	Suggested values
IPFLAG	Determine whether or not to generate chemist's printout	1 = Generate printout 0 = Suppress printout	1 = Chemist's printout is helpful in all cases
IDEBUG	Determine whether or not to generate debugging output	1 = Generate printout 0 = Suppress printout	0 = Printout necessary only when looking for errors
NTHIRDS	Set minimum # of scans for expected doublets	3,6,9 in units of 1/3 scan	3 = Expected distance as short possible
ITOM	Set neighborhood in histogram window for eluent detection	1,2 units of 1/3 scans	2 = Widest setting
MINNY	Set minimum histogram ion current for 1 to 4 peak eluents	Any integer greater than or euqal to 0	1000 currently used, setting greater than 0 recommended
MINTIC	Set minimum histogram ion current for eluents with more than 5 peaks	Any integer greater than or equal to 0	1000 currently used and recommended, critical that setting greater than zero is used
RATM	Minimum rate for eluent detection	Any real number greater than 0.0	0.0 = No minimum cutoff for peak rates appears necessary at this time
RATMXX	Eliminate column bleed from detected eluents by linear error ratio test	0.0 to 1.0	= .1, current value is .0756. It is critical that this parameter not be 0.0
ILEFT	Set number of scans required for increasing ion current prior to prospective model peak mode	1,2	2 = As wide a neighborhood about the mode as possible is recommended to ensure model accuracy
IRIGHT	Set number of scans required for decreasing ion current after prospective model mode	1,2,3	3 = Same as above
SATVAL	Tells CLEANUP instrument saturation value	All integers	= 200 below instrument saturation value (see text)

printouts, complete peak models, and decisions made as to whether the peak encountered was dismissed as noise, qualified as a singlet eluant, or whether the doublet resolver was invoked. With an average of 1 page of printout per eluant detected, the full printout for some test runs has frequently exceeded 200 pages. Although this information proved very helpful in finding some bugs in CLEANUP, we feel that unless thre is a specific need, this diagnostic output should be suppressed.

The first of the parameters affecting output spectra (NTHIRD) determines the closest distance which CLEANUP expects between neighboring eluants. Once the CLEANUP program detects an eluant from histograms of the ion current, it looks ahead in the histogram to determine if another eluant is in the vicinity just ahead. Although the variable NTHIRD is given in units of thirds of scans, only three values make a difference in terms of CLEANUP internal calculations. A value for NTHIRD of 3 means that neighboring eluants are expected no closer than 1 scan away, 6 means no closer than 2 scans, and 9 means that neighboring eluants are expected no closer than 3 scans from each other. The function of NTHIRD is shown graphically in Figure 18. From a theoretical point of view, there is no reason why this parameter should not be set to 3, setting the CLEANUP program to look for doublets within the finest possible grid. The danger of using a coarser setting is that some close pairs of eluants could be interpreted by the CLEANUP program as singlets, resulting in incorrect peak model choices and the deletion of unknowns. Our experience with varying this parameter over the test run however, showed only a mild dependence of results on the expected minimum distance, with the number of eluants decreasing by only 5% from the finest to the coarsest possible setting.

The detection window size (ITOM), has two possible values; 1 and 2, corresponding to the number of histogram positions which must be less than the central maximum in order for an eluant to qualify for detection. This is shown graphically in Figure 19. Currently, the most stringent setting is being used, requiring that histograms of ion currents for 2 members on either side of the central position be lower than the central value in order for an eluant to be detected. Statistics on this

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NTHIRD>6

[————→

3<NTHIRD≤6

[————————→   HISTOGRAM REGIONS
                    SEARCHED AHEAD FOR
0≤NTHIRD≤3   NEXT ELUENT

[————————————————→

‾‾‾⌣‾‾‾
HISTOGRAM
POSITIONS WHERE
1ST ELUENT IS
DETECTED

4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

[————————→

REGION AHEAD
SEARCHED WITH
NTHIRD=9

4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

↑   ↑

ELUENT   NEXT NEIGHBORING
DETECTED   ELUENT
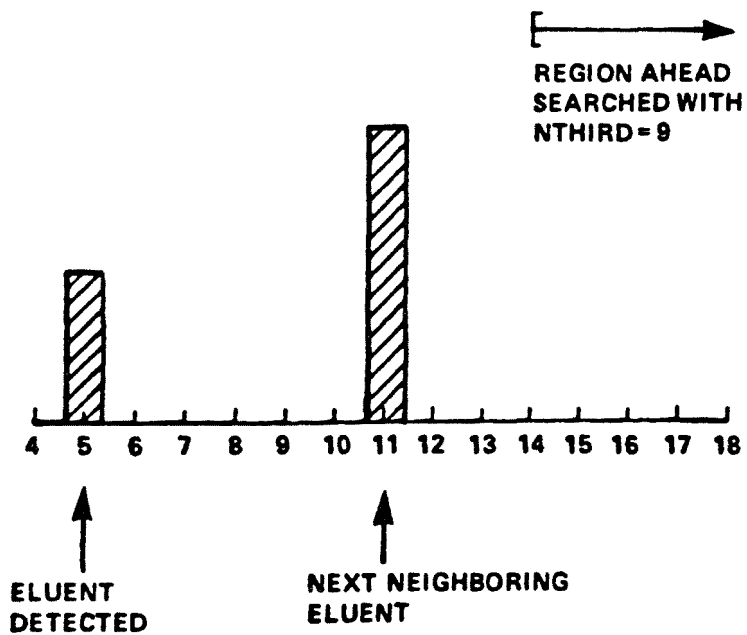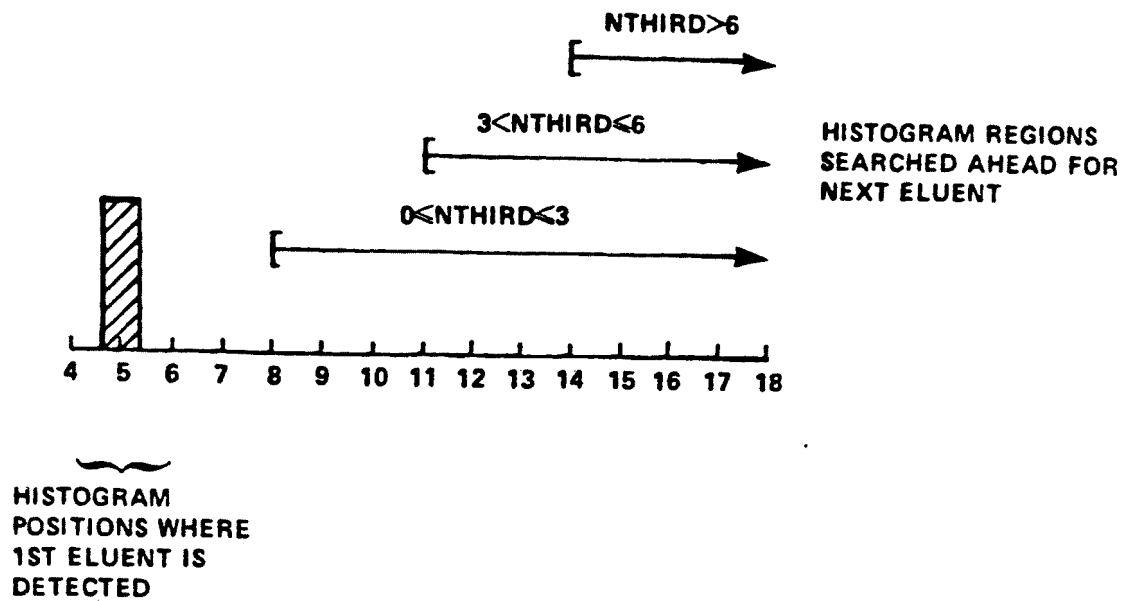
Example of Eluent Missed Due to Incorrect Setting of
NTHIRD Parameter

Figure 18. Graphic representation of possible settings of NTHIRD.
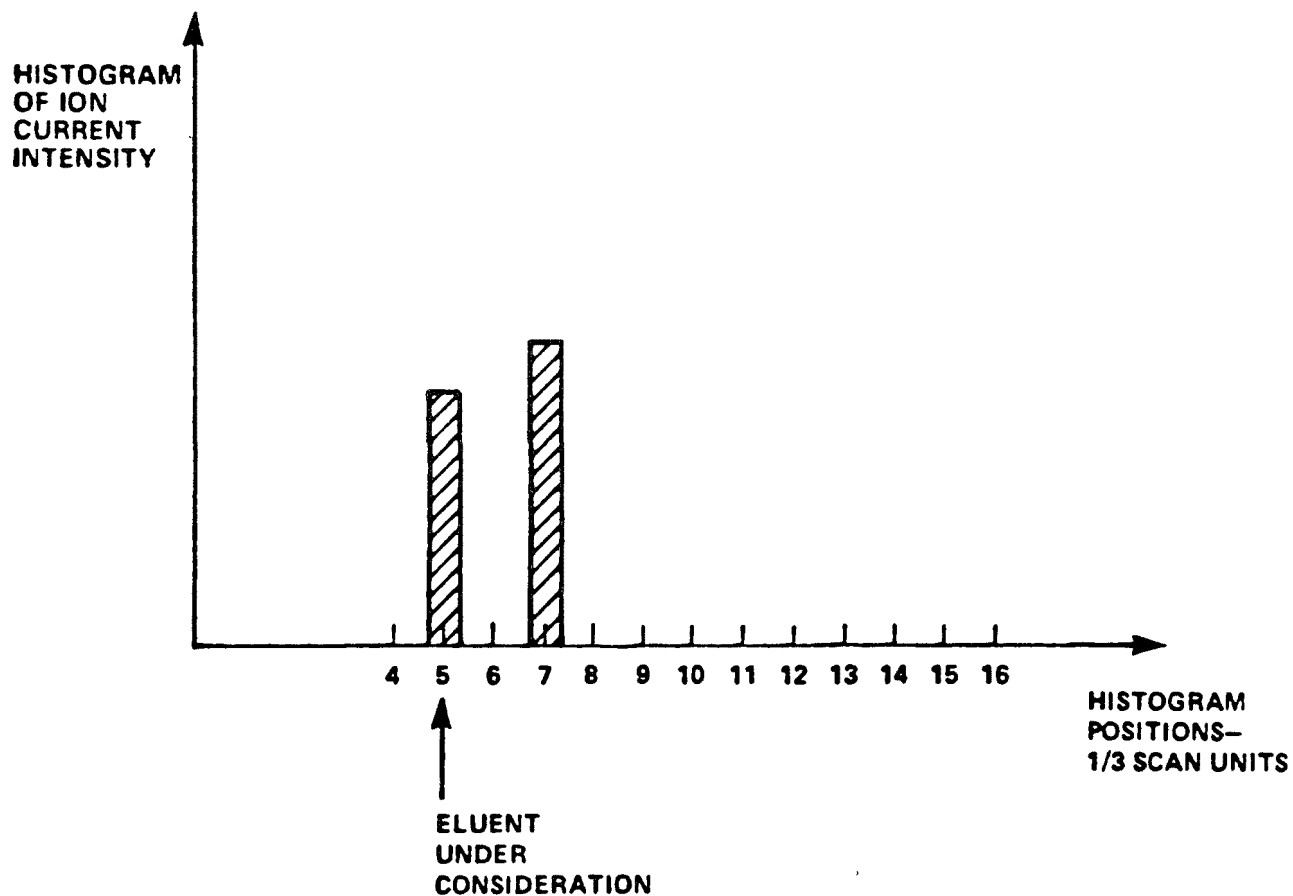
The ion at position 5 would be rejected with ITOM = 2 because of the neighboring eluent at position 7, whereas with ITOM = 1, it would be accepted.

Figure 19. Function of ITOM histogram window setting.

parameter were obtained, but in view of the fact that the CLEANUP algo-
rithm does not try to resolve doublets closer than 1 scan apart and
breaks down entirely for a distance of 1/3 scan, it was decided to keep
ITOM at its most rigorous value, 2.

The input parameters MINNY and MINTIC are minimum TIC histogram
intensity thresholds for eluant detection. It is important to note that
these ion currents are tested after background noise is subtracted.
There are two threshold settings, one for spectra containing very few
ions, (e.g. coronene), and one for spectra containing very few ions,
(e.g. coronene), and one for spectra containing 5 or more ions. In
addition, the reconstructed spectrum is required to have a total ion
current equal or greater than MINTIC otherwise it is not written to the
output file or noted in the chemist's printout. TIC threshold require-
ment was tested first by setting both parameters to 0, effectively
eliminating the TIC minimum cutoff. The result of this test was to more
than double the number of eluants detected by CLEANUP. Many of these
eluants when processed by the RTI search program were found to have less
than 5 compounds in the entire library which passed its two out of six
strongest peaks presearch test, indicating that the peaks consisted
mainly of noise. It is thus concluded that some TIC requirement is
necessary. We now believe that the value of 1000, presently used, is
too high. The optimum setting of this threshold must be determined
individually for every data system.

The parameter (RATM) sets a minimum sharpness on each model peak
before it can qualify as an eluant. The suggested value is 0, meaning
that no eluants are rejected, sharpness being positive definite. This
parameter was left at 0 for two reasons. First, there was no evidence
of spurious eluants being introduced due to insufficient sharpness, and
second, the distribution of sharpness values for the test run gave no
clues as to a best setting.

The function of the linear error ratio (RATMXX) is to remove those
single ion traces (fragmentograms) which contain column bleed. In order
to do this, a least squares fit to a straight line is calculated for an
11 scan window (5 scans on each side scan under consideration) and then

the ratio of the root mean square deviation of the peak shape about the line to the average value of the line is calculated (Figure 20). As indicated, peak shapes which are "too flat" can be eliminated by the error ratio criterion. Another useful property of the error ratio is that small peaks against very limited background noise will still be considered as eluants (b), whereas the same small ripple against a strong background would be dismissed as noise (c). We have varied the minimum error ratio requirement and we have demonstrated that the correct assignment of this variable is critical. The minimum error ratio requirement was reduced from the suggested .0756 to .002. Under these conditions CLEANUP found the same number of peaks as it had with the higher value found (the error ratio test is applied after an eluant has been detected in order to determine if reconstruction is worthwhile), but the CPU time required by the search program doubled and recognition performance markedly deteriorated. Extraneous peaks were admitted by CLEANUP, causing a large fraction of the unknowns to pass the presearch cycle of SEARCH and also causing misidentification in the search program due to the presence of those peaks.

The parameter ILEFT sets the number of scans which must show an increasing ion current prior to the mode in order for an ion fragmentogram to be considered as a model peak. Correspondingly, IRIGHT sets the number of scans required to show a decreasing ion current after the mode for model consideration. We feel that ILEFT and IRIGHT should be left at their maximum permissable values, 2 scans prior to and 3 scans after the mode. The CLEANUP algorithm achieves maximum efficiency when a typical singlet peak is 5 to 10 scans wide. If the scan rate is correctly "tuned" the most stringent setting for ILEFT and IRIGHT ensures that well-behaved individual ion traces are used as model peaks.

The parameter SATVAL defines the saturation value used by the program in order to determine when peaks are saturated and need to be reconstructed via a ratio approach. Although this number would be expected to be the theoretical maximum for the A/D convertor used in the data acquisition system, we have found it necessary to set SATVAL to a value slightly below the theoretical maximum. Thus, for the VARIAN

ION
CURRENT

PEAK FRAGMENTOGRAM (Pi, i=1,11)

$P_i \cdot \ell_i$

LEAST SQUARES FIT
STRAIGHT LINE (ℓ_i, i=1,11)

SCAN
NUMBER
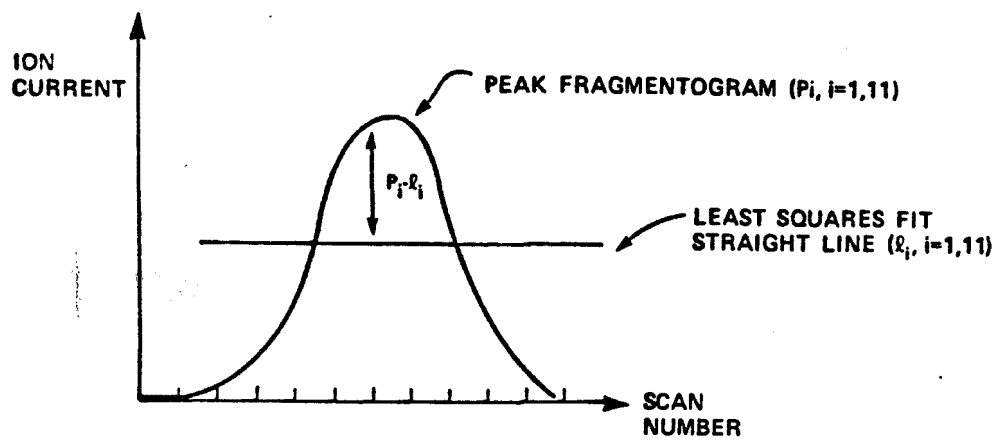
$$\text{ERROR RATIO} = \frac{\sqrt{\sum_{i=1}^{i=11} (P_i - \ell_i)^2}}{\sum_{i=1}^{i=11} \ell_i}$$

EXAMPLES:

(a)
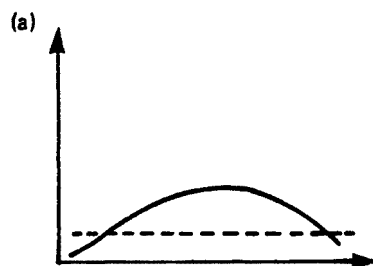
Peak thrown out because
error ratio is too low

(b)
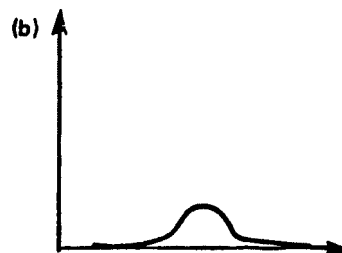
Small, relatively sharp peak
admitted because of small
denominator in error ratio

(c)
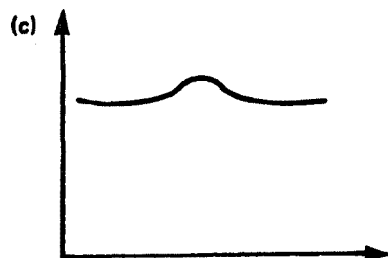
Same small peak here is thrown out
as noise because of large denominator
in linear error ratio

Figure 20.   Effects of linear error ratio.

system, the maximum A/D output is 32,767 (2^{15}-1), we currently have SATVAL set to 32,000. For unknown reasons, A/D convertors often register values less than their maximum for known, saturated peaks. In such cases, saturated peaks can inadvertently be eliminated entirely as background noise (Figure 21).

Again, the values for the parameters shown in Table 7 are satisfactory for VARIAN CH-7 data. It must be realized however, that these values are instrument and data dependent, and optimum values for any particular data system must be determined empirically by adjustment of parameters, which will require some experience gained only with time.

ION
CURRENT

THEORETICAL DETECTOR
MAXIMUM

a

b

99% OF THEORETICAL
DETECTOR MAXIMUM

SCAN NUMBER
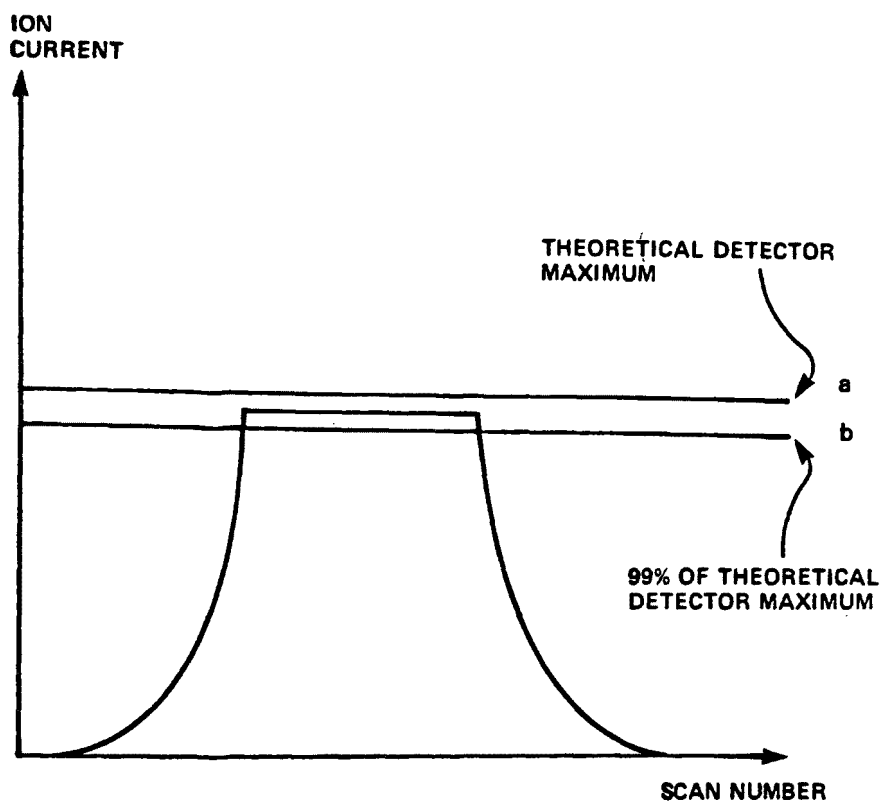
With SATVAL setting at value (a), the saturated peak is constructed by CLEANUP to
be entirely background noise, but with a slightly reduced setting (b) for SATVAL,
the peak is recognized as saturated and handled by the correct routines.

Figure 21. Effect of SATVAL on CLEANUP.

SECTION 5

IMPLEMENTATION OF THE CLEANUP PROGRAM ON THE UNIVAC COMPUTER

Phase III of this contract consisted of making the CLEANUP program developed at RTI operational on the UNIVAC computer located at EPA. This work was carried out simultaneously with some improvements being made in the organization of the data formats in CLEANUP.

Because RTI's and EPA's environment for using the CLEANUP program are similar, it was decided to use the same CLEANUP source version for each. The general plan was to change the READ and WRITE statements inside CLEANUP to subroutine calls and then write a set of I/O subroutines for EPA and later a set of I/O routines for RTI's system.

There were two advantages to this approach. First, the CLEANUP program would require substantially less modification. In addition, if any bugs were to occur in CLEANUP in the future, it would be possible to investigate the problem by carrying out a debugging run at TUCC. This would verify whether the bug was a system oriented problem or an algorithm deficiency inside CLEANUP proper. If the problem was indeed a bug in CLEANUP, it could be corrected at TUCC. Systems problems at the UNIVAC would be corrected there. Modules required for these programs are shown on Figure 22. The code to be delivered to EPA consists of sections 1, 2 and 3. A short description of each of these modules follows.

Some minor modifications to the original CLEANUP program besides changing READ and WRITE statements were made. The most important of these was to expand the CLEANUP program so that it could process multiple runs on the same tape data set. To include this facility, the routines PARDIR (reading in the CLEANUP input parameters) and SETRUG (initializing the 14 spectra window with the first 13 spectra) had to be repositioned and rewritten.
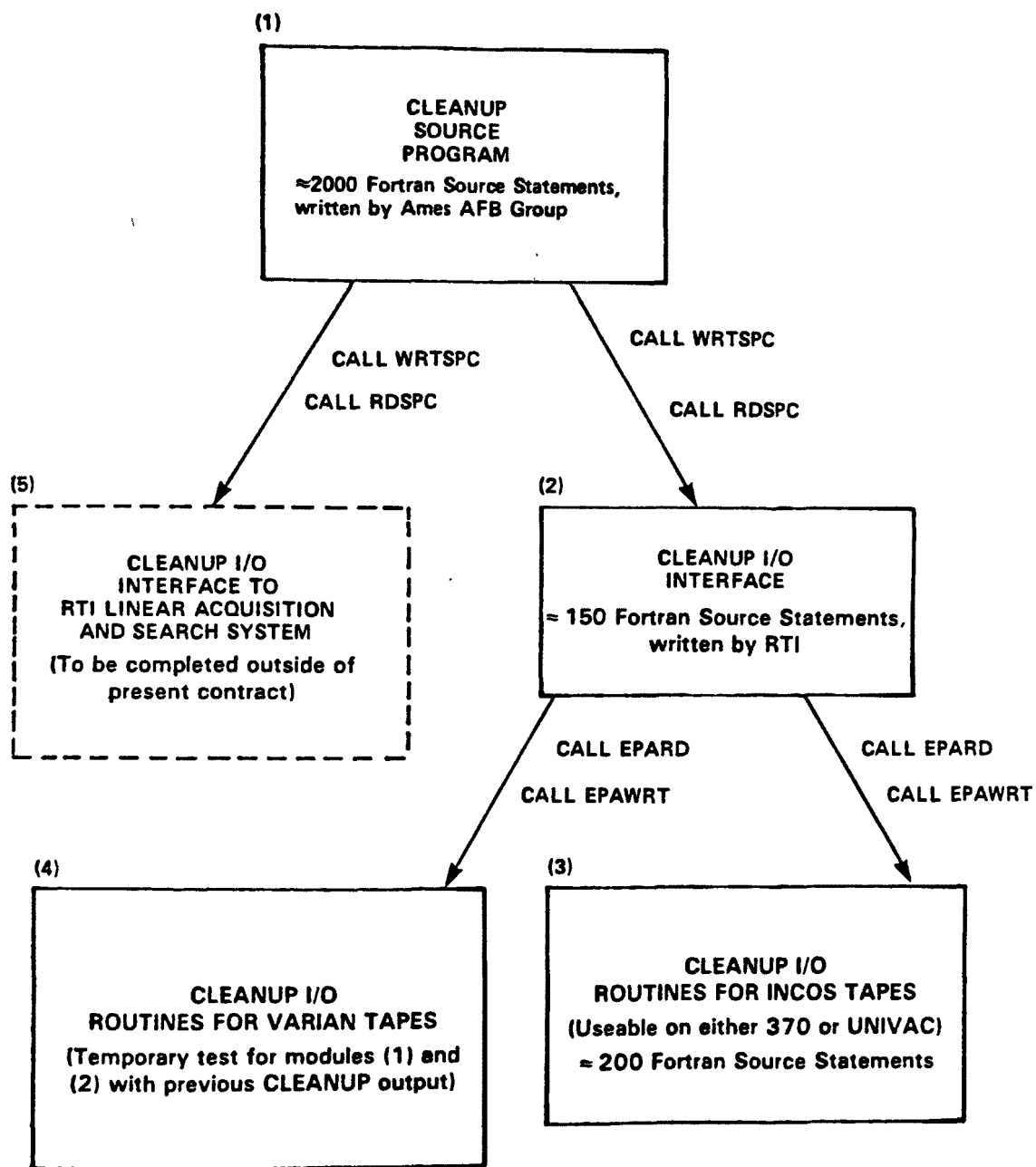
Figure 22. Modules required for transfer of CLEANUP program to UNIVAC.

Rather than have CLEANUP call the I/O routines directly, it was decided to create an intermediate step consisting of an I/O interface called by CLEANUP which would in turn call the I/O routines. This was necessary because the only data used by CLEANUP for internal calculations are individual ion intensities while the INCOS tape data contained much additional identification information. Although not used by CLEANUP, these items were carried along to be able to write output spectra in the same format as on the original input tape. The interface served the dual function of keeping track of data not used directly inside CLEANUP and of making the I/O routines more versatile for use with other tasks.

The modification of the CLEANUP program involved roughly 500 statements: 100 statements for the rewritten routines inside CLEANUP, 200 statements for the I/O interface, and 200 statements for the I/O routines. To assure accuracy and quality control, several cross checks were made.

In order to insure the correctness of the modified CLEANUP source (1) and the I/O interface (2) a temporary set of I/O routines for reading the VARIAN CH 7 data (4) were written. These routines purposefully had exactly the same calling arguments as the INCOS tape I/O routines (3). These routines were written in standard FORTRAN and involved little more than READ and WRITE statements. It was then possible to test CLEANUP and the I/O interface on one of the eight trial runs. The prototype run was much more difficult to achieve than anticipated, mainly due to communication problems between the main CLEANUP source module and the I/O interface. However, because everything was in strict FORTRAN it was possible to use the WATFIV interpreter to find the majority of the CLEANUP bugs. The WATFIV interpreter again proved itself invaluable, not only in solving otherwise very subtle problems but also by insuring machine independence of the code. Thus, output of the CLEANUP source with the new I/O interface was verified against earlier output from the version of the CLEANUP program which was "spliced" into the RTI system.

It remained to test out the I/O routines (3) on an INCOS tape data set. After we were convinced that the I/O routines were operating properly, a program was written to generate a TIC plot of the first INCOS test run with the aid of the UNC plotter facility and the TUCC plotter routines. A reproduction of this plot is shown in Figure 23. This plot confirms that the data were correctly read and interpreted by the program.

Initially, running CLEANUP with INCOS test data on the TUCC IBM/370 detected only 8 eluants in the entire run. Closer examination of the data revealed that the average peak width for the INCOS runs extended over some 25 scans. Since the CLEANUP program derives its model singlets from a 7 scan window, not enough peak profile was available to obtain a good model shape (Figure 24). The simplest solution to this problem was to incorporate another parameter into the CLEANUP program which would average over a specified number of input spectra before any internal calculations were made. Once this modification was incorporated into CLEANUP, the same run was processed again, averaging over three spectra at a time. The results were much improved, showing a total of 72 eluants detected in the run (Figure 25).

After verification that the scan numbers of detected eluants agreed with the TIC plot (Figure 23) and checking the masses and intensities of detected eluants on the output tape against CLEANUP diagnostic printout, the task of duplicating this run with the same input tape on the UNIVAC computer was undertaken. A card copy of the CLEANUP source code was generated on the TUCC 370 and transported to the EPA UNIVAC when the source was recompiled and cross checking of its output. The chemist's printout of the test run on the UNIVAC is shown in Figure 26. The small discrepancies between this printout and the chemist's printout generated at TUCC are of a round-off type arising from hardware differences (i.e. word length, floating point arithmetic) between the two machines. These differences are too small to affect the performance of CLEANUP.

A second problem of greater concern occurred when trying to process multiple runs on a single tape with the EPA UNIVAC. Problems were encountered either when attempting to write a file mark at the end of
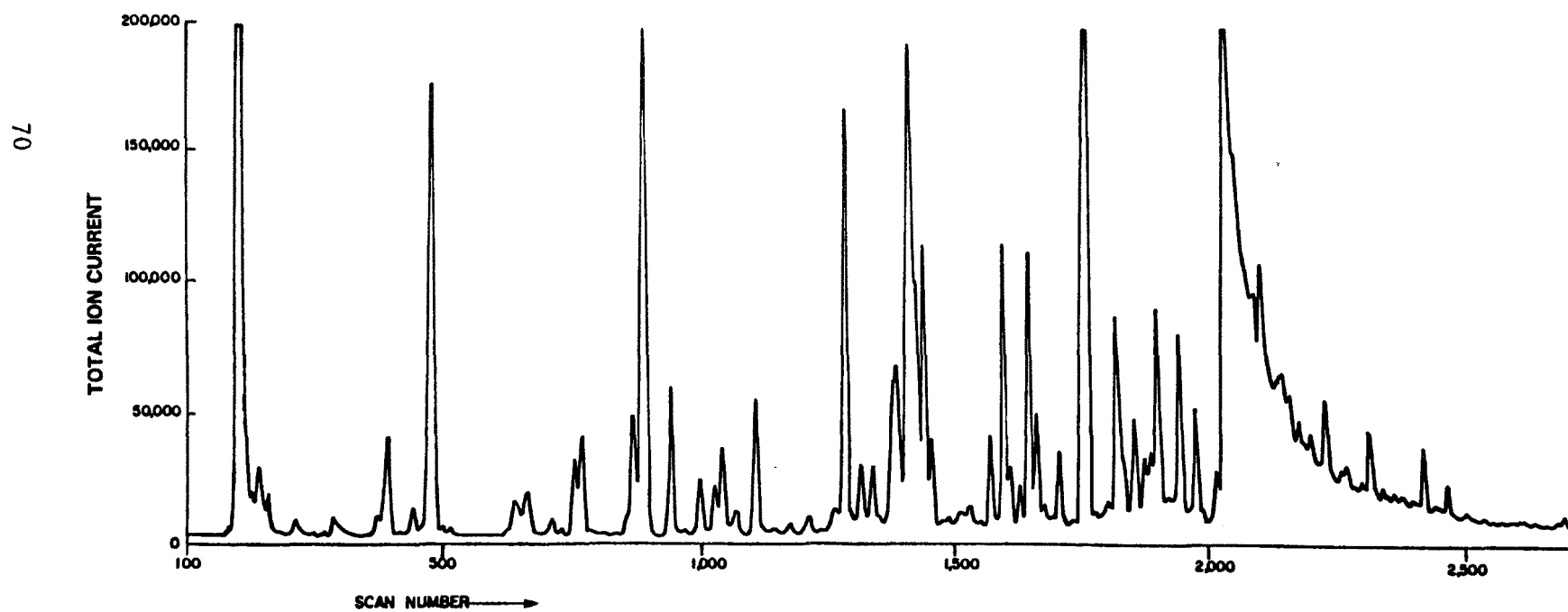
Figure 23.   Raw TIC of INCOS test data.

ION
CURRENT   MAXIMUM

[ ]
CLEANUP DETECTION WINDOW

SCAN NUMBER
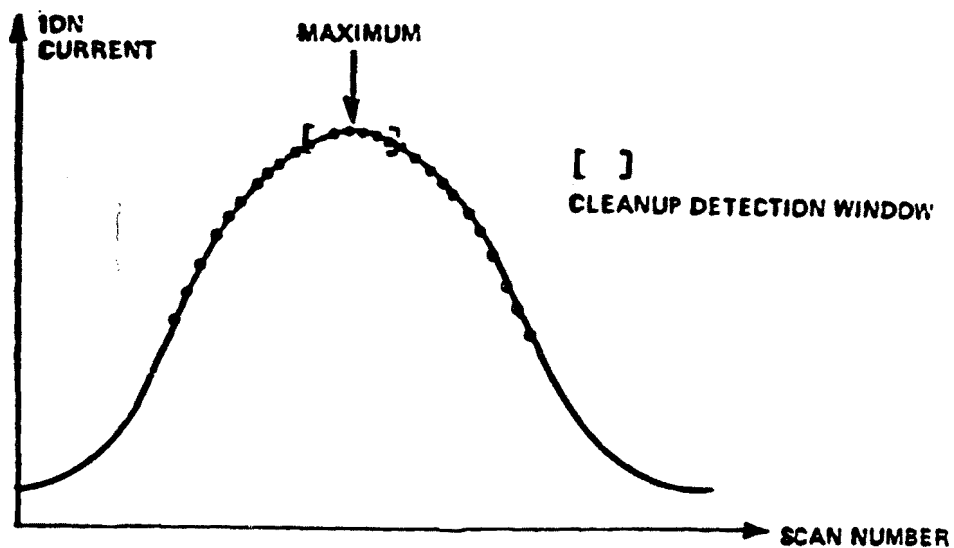
VALID PEAK DISCARDED DUE TO FAILURE OF LINEAR ERROR RATIO TEST

ION
CURRENT

[ ]
DETECTION WINDOW

SCAN NUMBER
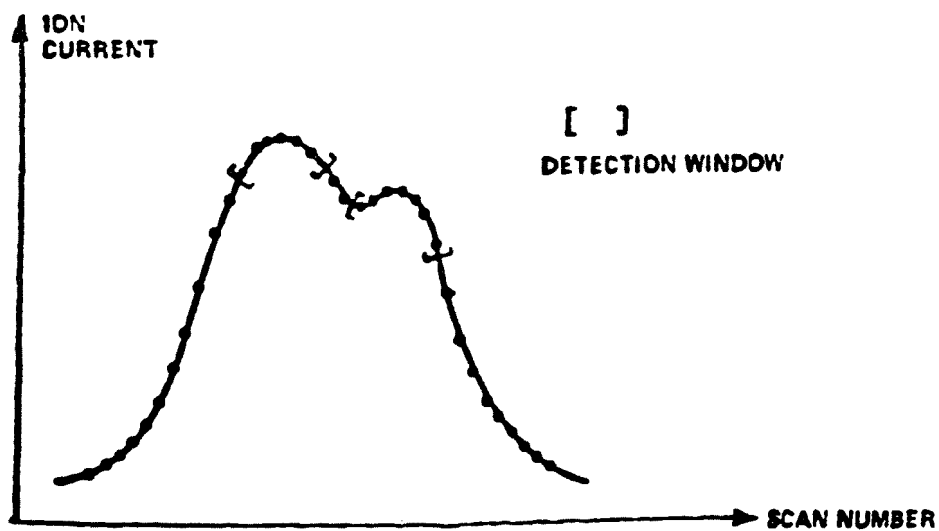
DOUBLET INCORRECTLY INTERPRETED AS TWO SINGLETS

Figure 24. Possible consequences of scan rate too rapid for CLEANUP.

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SLOT	SPEC.#	TUTION	TICRAT	MAX. AMP	DOUBLET?	SAT. PEAKS
1	85	1936.	31	1775.	NO	0
2	97	166999.	57	104876.	NO	0
3	130	2347.	13	1197.	YES	0
4	142	14250.	47	4738.	NO	0
5	145	14453.	51	8170.	NO	0
6	169	2224.	33	1366.	NO	0
7	217	4049.	54	2213.	NO	0
8	442	5897.	44	2573.	NO	0
9	475	147816.	92	53347.	NO	0
10	499	1770.	25	857.	NO	0
11	658	15973.	72	5954.	NO	0
12	709	6051.	65	1896.	NO	0
13	856	5265.	45	1925.	YES	0
14	866	41455.	99	9156.	NO	0
15	886	166097.	91	41310.	NO	0
16	904	1142.	23	561.	NO	0
17	940	47802.	98	19710.	NO	0
18	967	1046.	18	359.	NO	0
19	1066	4617.	37	1066.	NO	0
20	1108	44296.	99	13477.	NO	0
21	1150	1070.	18	400.	NO	0
22	1216	4953.	51	1057.	NO	0
23	1265	87503.	59	24632.	YES	0
24	1288	69335.	55	24065.	NO	0
25	1321	18167.	69	5751.	NO	0
26	1361	7455.	12	4126.	YES	0
27	1384	35357.	59	10480.	NO	0
28	1387	3959.	6	2111.	NO	0
29	1390	32665.	50	15485.	NO	0
30	1417	116059.	73	32707.	YES	0
31	1420	16945.	13	8773.	YES	0
32	1429	61522.	67	12418.	NO	0
33	1435	5456.	13	2191.	NO	0
34	1444	74565.	73	18173.	NO	0
35	1513	3418.	26	950.	YES	0
36	1522	2746.	24	520.	YES	0
37	1534	4649.	33	2156.	NO	0
38	1576	24853.	97	12032.	NO	0
39	1600	60520.	61	18903.	NO	0
40	1630	11792.	64	4708.	NO	0
41	1648	1246.	1	677.	NO	0
42	1651	77545.	84	16005.	NO	0
43	1666	19490.	45	11114.	NO	0
44	1681	2005.	18	665.	NO	0
45	1711	24254.	72	7455.	NO	0
46	1759	440051.	90	68275.	NO	0
47	1822	69229.	98	21607.	YES	0
48	1831	14281.	44	2935.	NO	0
49	1837	7724.	29	4362.	NO	0
50	1876	1203.	3	491.	YES	0
51	1897	4384.	6	1065.	YES	0
52	1903	60098.	93	8852.	NO	0
53	1906	10533.	27	3897.	NO	0
54	1939	4987.	11	909.	YES	0
55	1945	56164.	88	15042.	NO	0
56	1978	36425.	95	9039.	NO	0
57	2020	11452.	49	3519.	YES	0
58	2029	227926.	81	32760.	NO	0
59	2050	5058.	2	1514.	NO	0
60	2104	31191.	31	7311.	NO	0

Figure 25. Chemist's printout of EPA test run generated at TUCC.

SLOT	SPEC.#	TOTION	TICRAT	MAX. AMP	DOUBLET?	SAT. PEAKS
1	85	1938.	31	1775.	NO	0
2	97	167000.	57	104876.	NO	0
3	130	2347.	13	1197.	YES	0
4	142	14250.	47	4738.	NO	0
5	145	14453.	51	8170.	NO	0
6	169	2224.	33	1366.	NO	0
7	217	4049.	54	2213.	NO	0
8	442	5897.	44	2573.	NO	0
9	475	147816.	92	53347.	NO	0
10	499	1770.	25	857.	NO	0
11	658	13973.	72	5954.	NO	0
12	709	6052.	65	1898.	NO	0
13	856	5285.	45	1925.	YES	0
14	868	41455.	99	9156.	NO	0
15	886	166097.	91	41310.	NO	0
16	904	1143.	23	562.	NO	0
17	940	47802.	98	19716.	NO	0
18	967	1046.	18	359.	NO	0
19	1066	4617.	37	1068.	NO	0
20	1108	44296.	99	13477.	NO	0
21	1150	1070.	18	400.	NO	0
22	1216	4953.	51	1057.	NO	0
23	1285	87303.	59	24832.	YES	0
24	1288	69335.	55	24065.	NO	0
25	1321	18167.	69	5751.	NO	0
26	1381	7455.	12	4126.	YES	0
27	1384	35358.	59	10481.	NO	0
28	1387	3959.	6	2111.	NO	0
29	1390	32685.	50	15483.	NO	0
30	1417	116839.	73	32767.	YES	0
31	1420	16945.	13	8773.	YES	0
32	1429	61523.	67	12418.	NO	0
33	1435	5456.	13	2191.	NO	0
34	1444	74385.	73	18173.	NO	0
35	1513	3418.	28	950.	YES	0
36	1522	2746.	24	520.	YES	0
37	1534	4649.	33	2156.	NO	0
38	1576	29853.	97	12032.	NO	0
39	1600	60520.	61	18903.	NO	0
40	1636	11792.	64	4708.	NO	0
41	1648	1246.	1.	677.	NO	0
42	1651	77546.	84	16005.	NO	0
43	1666	19490.	45	11114.	NO	0
44	1681	2603.	18	663.	NO	0
45	1711	24234.	72	7455.	NO	0
46	1759	440632.	90	68274.	NO	0
47	1822	69229.	98	21607.	YES	0
48	1831	14281.	44	2935.	NO	0
49	1837	7724.	29	4362.	NO	0
50	1876	1203.	3	491.	YES	0
51	1897	4384.	6	1083.	YES	0
52	1903	60098.	93	8852.	NO	0
53	1906	10533.	27	3897.	NO	0
54	1939	4987.	11	909.	YES	0
55	1945	56184.	88	15042.	NO	0
56	1978	36425.	95	9039.	NO	0
57	2020	11452.	49	3519.	YES	0
58	2029	227926.	81	32760.	NO	0
59	2050	3858.	2	1514.	NO	0
60	2104	31191.	31	7311.	NO	0
61	2134	2738.	4	1084.	YES	0
62	2140	1990.	3	850.	NO	0
63	2179	8014.	19	3174.	NO	0
64	2200	2661.	6	607.	NO	0
65	2227	14861.	27	3754.	NO	0
66	2266	5288.	17	2042.	NO	0
67	2314	18434.	43	5317.	NO	0
68	2341	2516.	12	843.	NO	0
69	2422	21799.	84	10656.	NO	0
70	2455	1045.	7	657.	NO	0
71	2467	10041.	43	2636.	NO	0
72	2698	3222.	29	835.	NO	0

Figure 26. Chemist's printout of EPA test run.

the output cleaned up spectra tape or when attempting to locate the beginning
of a subsequent run on the input test tape. Because it was possible to detect
file marks separating the three runs on the EPA test tape at TUCC with no
difficulty, it was concluded that the problem lay with the UNIVAC. Notwith-
standing that the systems staff for the EPA UNIVAC have been alerted to these
difficulties, we recommend that for the present CLEANUP runs on the UNIVAC be
limited to one input and output file per tape.

SECTION 6

USER DESCRIPTION OF PROGRAM OPERATION

The final phase of implementing CLEANUP in the EPA environment consisted of testing the output tape written by the UNIVAC on the contracting agency's INCOS acquisition system. Although numerous problems were encountered, they were all of a systems oriented nature (incorrect tape density, incomplete format information, etc.) which commonly occur with machine transfer. No internal algorithm changes to the CLEANUP program were necessary in order to successfully read the test tape and obtain plausible output spectra with the INCOS software.

A user oriented description for running CLEANUP on the UNIVAC follows. To execute CLEANUP at the UNIVAC, it is necessary to deliver two tapes (one containing the INCOS raw input spectra and one for the output spectra) along with a card deck containing program control information (Figure 27). Cards 1 through 5 and 19 through 25 comprise the Executive Control Language necessary for the UNIVAC system to recognize and run the CLEANUP program. Of these, it is necessary to change the underlined portions of cards 19 and 20 with each run because they specify the tape serial numbers for CLEANUP to use. Cards 21 and 22 specify the positions of the data sets on the input and output tapes - in this example the input is read from the second file of tape B003KK and the output is written to the third file of tape B334KK. Cards 21 and 22 should be omitted if only one run is present on the input tape, and the cleaned up run is to be written on the beginning of the output tape. Card 1 - the "run" card contains the job name (CLNP) and the maximum time estimate in minutes (5). Although none of the present tests exceeded three minutes, it is conceivable that an increase of the time requirement could become necessary in the future.

```
@RUN 2uCLNP/45/2,640265A010/KJK,5A010,5                              1
@PASSWD  KJK                                                         2
@ASG,A A.                                                            3
@ASG,T 4.        . CONTAINS THE CONTROL CARD DATA                    4
@DATA,I 4.        . THE ACTUAL CONTROL CARD DATA FOLLOWS             5
1       CLEANUP PRINT FLAG (IN I1)                                   6
0       DEBUG PRINT SWITCH IN I1 (0=NO,1=YES)                        7
 3      NUMBER OF INPUT SPECTRA TO AVERAGE (IN I2)                   8
 6      MINIMUM THIRDS BETWEEN ELLUANTS (IN I1)                      9
   2       DETECTION WINDOW (IN I4)                                 10
   1000       MINIMUM FOR LESS THAN 5 PEAKS (IN I6)                 11
   1000       MINIMUM FOR MORE THAN 4 PEAKS (IN I6)                 12
    .0000       MINIMUM QUALIFYING RATE (IN F8.4)                   13
    .0350       ERROR RATIO (IN F8.4)                               14
    2       POINTS TO LEFT OF MODE (IN I3)                          15
    3       POINTS TO RIGHT OF MODE (IN I3)                         16
130000       SATURATION VALUE (IN F6.0)                             17
@END                                                                18
@ASG,TJH 7.,16D///////0,B003KK         . INPUT TAPE                 19
@ASG,TJH/N 9.,16D///////0,B334KK       . OUTPUT TAPE                20
@MOVE 7.,1 .SKIP 1 FILE ON INPUT TAPE-USE 2ND FILE                  21*
@MOVE 9.,2 .SKIP 2 FILES ON OUTPUT TAPE-USE 3RD FILE                22*
@XQT,F A.CLEANUP                                                    23
@MARK 9.            . PUT A 'SAFETY' END OF FILE ON OUTPUT TAPE     24
@FIN               . END OF RUN                                     25
```

*omit until multiple run processing is implemented.

Figure 27.   Example of CLEANUP control cards for EPA UNIVAC.

Cards 6 through 17 comprise the control cards used by the CLEANUP program. It is important to note that the variables shown here have been optimized with respect to the EPA test data taken on the INCOS system and hence differ from those in Table 7 which were optimized with respect to the VARIAN CH-7 at RTI. The most important difference is the additional control card (card 8) which instructs CLEANUP to average over 3 spectra. Also the instrument saturation value was changed to 130,000 (card 17), the minimum thirds between ellutants was increased from 3 to 6 (card 9), and the error ratio requirement was reduced from .0756 to .035 (card 14). The changes in minimum thirds and error ratio were made in order to accommodate the wider peak width and smoother data generated on the INCOS system.

SECTION 7

DELIVERY TO EPA

Accompanying this report are listings of the CLEANUP program which currently is being run on the UNIVAC, completing Phase IV of the contract. A backup tape of the same programs will be kept by RTI as well as the version of CLEANUP at TUCC which runs on INCOS tapes.

It still will be necessary for the contracting agency to carry out a series of test runs in order to determine the best operating parameters for CLEANUP. The system will respond differently to data derived from different mass spectrometers, as well as data run under differing GC conditions.

The program affords considerable flexibility in operation by the suitable adjustment of variable input parameters. These will still need to be exercised until optimum operational conditions are determined.

REFERENCES

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3. "Reconstructed Mass Spectra. A Novel Approach for the Utilization of Gas Chromatograph-Mass Spectrometer Data." J. E. Biller and K. Biemann, Anal. Lett., 7, 515 (1974).

4. "Extraction of Mass Spectra Free of Background and Neighboring Component Contributions from Gas Chromatography/Mass Spectrometry Data," R. G. Dromey, M. J. Stefik, T. C. Rindfleisch, and A. M. Duffield, Anal. Chem., 48, 1368 (1976).

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APPENDIX A
CLEANUP SOURCE LISTING

.

```
      SUBROUTINE EPARD                                              00035690
C                                                                   00035700
C     THIS ENTRY POINT READS ONE SCAN'S WORTH OF DATA PER CALL AND RETURNS00035710
C     IT TO THE CALLING ROUTINE IN COMMON BLOCKS IHDR AND INDATA.   00035720
C                                                                   00035730
      COMMON /HDR1/ NAME,HDRFLG,DATE,RUNHR,RUNMIN                   00035740
      COMMON /HDR2/ SAMPID,INAM                                     00035750
      COMMON /HDR3/ RUNCON,SECSCN                                   00035760
      COMMON /HDR4/ BUF4,LOPMAS,HIPMAS                              00035770
      COMMON /IHDR/ JNAM,ISCN,IDBUF,IDHR,IDMIN,IRTMIN,IRTSEC,INMBAS,00035780
     * IRBAS,IRTIC                                                  00035790
      COMMON /INDATA/ INBUF,INSEQ,NIN                               00035800
      COMMON /OHDR/ ONAM,OSCN,ODBUF,ODHR,ODMIN,ORTMIN,ORTSEC,ONMBAS,00035810
     * ORBAS,ORTIC                                                  00035820
      COMMON /OTDATA/ OTBUFF,OTSEQ,NOUT                              0003583
      COMMON /FLAGS/ EOF                                            00035840
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPRT3,IIN,IOUT                00035850
      COMMON /IOBUF/ ITBUF1,CNTIN,CNTOUT,IOERR,ITBUF2               00035860
      INTEGER*4 NAME(3),HDRFLG,DATE(2),RUNHR,RUNMIN,SAMPID(16),INAM(2),00035870
     * RUNCON(16),BUF4(11),LOPMAS,HIPMAS,JNAM(3),ONAM(3),ISCN,OSCN,00035880
     * IDBUF(2),ODBUF(2),IDHR,ODHR,IDMIN,ODMIN,IRTMIN,ORTMIN,IRTSEC,00035890
     * ORTSEC,INMBAS,ONMBAS,EOF                                     00035900
     *,INSEQ,OTSEQ,NIN,NOUT,INBUF(411),OTBUFF(411)                 00035910
      INTEGER*4 RCDLEN/80/,CNTIN,CNTOUT,ITBUF1(20),IBLANK/4H     /, 00035920
     * INSPC(26),IDD(11),OTSPC(26),SCNEND/0/,ITBUF2(20)            00035930
      INTEGER*4 OTSPCX(3,26),OTSEQX,OTSEQY                          00035940
      REAL*4 SECSCN,ORBAS,IRBAS,IRTIC,ORTIC                         00035950
C                                                                   00035960
C     SET SCAN FLAG, COUNTER.                                       00035970
C                                                                   00035980
      SCNEND=0                                                      00035990
      NIN=0                                                         00036000
C                                                                   00036010
C     CLEAR TRANSFER ARRAY IN 'INDATA' BLOCK.                       00036020
C                                                                   00036030
      DO 5 I=1,411                                                  00036040
    5 INBUF(I)=0                                                    00036050
C                                                                   00036060
C     CALL BLKRD TO BRING A LOGICAL RECORD INTO THE BUFFER.         00036070
C                                                                   00036080
      CALL BLKRD                                                    00036090
      IF (IOERR.LT.0) GO TO 1000                                   00036100
C                                                                   00036110
C     DECODE A LOGICAL RECORD (ASSUMED TO BE A SCAN HEADER).        00036120
C                                                                   00036190
      DECODE(RCDLEN,5000,ITBUF1) JNAM,IDD(1),ISCN,IDD(2),IDBUF,IDHR,
     * IDD(3),IDMIN,IDD(4),IDD(5),IRTMIN,IDD(6),                   00036200
     * IRTSEC,IDD(7),IDD(8),INMBAS,IDD(9),IRBAS,IDD(10),IDD(11),IRTIC 00036210
C                                                                   00036220
 5000 FORMAT(3A4,A1,I5,A2,2A4,I3,A1,I2,A4,A1,I3,A1,I2,A4,A2,I4,A1,F9.0,00036230
     * A4,A1,F10.0)                                                 00036240
C                                                                   00036250
C     STOP IF NEW HEADER FOR RUN IS ENCOUNTERED.  (ISCN=0)          00036260
C                                                                   00036270
      IF (ISCN.EQ.0) GO TO 110                                     00036280
C                                                                   00036290
C     HANDLE SPECTRUM RECORD(S).  AT LEAST ONE IS ASSUMED TO BE PRESENT.00036300
C
```

```
C                                                                    00036310
C     CHECK BUFFER VIA POINTERS TO DETERMINE AMOUNT OF REMAINING DATA. 00036320
C                                                                    00036330
C     RETURN HERE IF MORE THAN ONE SCAN RECORD.                      00036340
C                                                                    00036350
   45 CALL BLKRD                                                     00036360
      IF (IOERR.LT.0) GO TO 2000                                     00036370
C                                                                    00036380
C     DECODE A SPECTRUM RECORD.                                      00036390
C                                                                    00036400
   80 CONTINUE                                                       00036430
C                                                                    00036450
      DECODE(RCDLEN,5005,ITBUF1) INSPC,INSEQ                         00036460
C                                                                    00036470
 5005 FORMAT(26I3,I2)                                                00036480
C                                                                    00036490
C     STORE THIS RECORD'S DATA IN INBUF USING SPECTRUM MASS AS INDEX OF IN00036500
C                                                                    00036510
      DO 86 I=1,25,2                                                 00036520
      J=I+1                                                          00036530
      L=INSPC(I)                                                     00036540
      IF (L.NE.0) GO TO 83                                           00036550
      SCNEND=1                                                       00036560
      GO TO 86                                                       00036570
   83 L=L-39                                                         00036580
      IF (L.LT.1.OR.L.GT.411) GO TO 86                               00036590
      INBUF(L)=INSPC(J)                                              00036600
      NIN=NIN+1                                                      00036610
   86 CONTINUE                                                       00036620
C                                                                    00036630
C     CHECK WHETHER END-OF-SCAN ENCOUNTERED (MASS VALUE = 0).        00036640
C                                                                    00036650
      IF (SCNEND.EQ.0) GO TO 45                                      00036660
C                                                                    00036670
C     RETURN WHEN SCAN ENDS (SCNEND = 1).                            00036680
C                                                                    00036690
      SCNCNT=SCNCNT+1                                                00036700
      RETURN                                                         00036710
C                                                                    00036720
C     ENTRY POINT FOR WRITING OUTPUT TAPE FOR INCOS USE.             00036730
C                                                                    00036740
      ENTRY EPAWRT                                                   00036750
C                                                                    00036760
C     WRITE SCAN HEADER TO TEMPORARY BUFFER FROM COMMON BLOCK OHDR.  00036770
C                                                                    00036780
C                                                                    00036850
      ENCODE(RCDLEN,5000,ITBUF2) ONAM,IDD(1),OSCN,IDD(2),ODBUF,ODHR, 00036190
     * IDD(3),ODMIN,IDD(4),IDD(5),ORTMIN,IDD(6),
     * ORTSEC,IDD(7),IDD(8),ONMBAS,IDD(9),ORBAS,IDD(10),IDD(11),ORTIC 00036200
C                                                                    00036880
C                                                                    00036890
C     MOVE ENCODED HEADER RECORD TO OUTPUT BUFFER.  WRITE A FULL BUFFER AS00036900
C     REQUIRED VIA NTRAN (CALLED FROM SUBROUTINE BLKWRT).            00036910
C                                                                    00036920
      CALL BLKWRT                                                    00036930
C                                                                    00036940
C     STORE OTBUFF (PROCESSED OUTPUT SCAN) IN OTSPC AS MANY TIMES AS  00036950
```

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```
C      WHEN OTSPC IS FULL, IT IS ENCODED INTO ITBUF2.              00036970
C                                                                  00036980
       J=-1                                                        00036990
       OTSEQ=1                                                     00037000
       DO 87 I=1,26
       OTSPC(I)=0
       DO 87 M=1,3
   87 OTSPCX(M,I)=0
       DO 100 I=1,411                                              00037010
C                                                                  00037020
C      LOOP ENDING AT 100 USES J & L AS INDICES TO OTSPC;          00037030
C                                                                  00037040
C      DATA IN OTSPC ARE:                                          00037050
C         MASS (I+39, WHERE 'I' IS THE INDEX OF OTBUFF);           00037060
C      AND INTENSITY, THE CONTENTS OF OTBUFF(I).                   00037070
C                                                                  00037080
C      MASS IS STORED IN OTSPC(J) AND INTENSITY IS STORED IN OTBUFF(L),  00037090
C         WHERE L = J + 1.                                         00037100
C                                                                  00037110
       IF (OTBUFF(I).LE.0) GO TO 100                               00037120
       J=J+2                                                       00037130
       L=J+1                                                       00037140
       OTSPC(J)=I+39                                               00037150
       OTSPC(L)=OTBUFF(I)                                          00037160
       IF (J.LT.25) GO TO 100                                      00037170
C                                                                  00037180
C      ENCODE SCAN DATA FROM OTSPC TO ITBUF2.                      00037190
C                                                                  00037200
C                                                                  00037250
       DO 88 M=1,26
       I1=OTSPC(M)
       I2=I1/100
       I3=I1/10-I2*10
       I4=I1-I3*10-I2*100
       OTSPCX(1,M)=I2
       OTSPCX(2,M)=I3
   88 OTSPCX(3,M)=I4
       OTSEQX=OTSEQ/10
       OTSEQY=OTSEQ-OTSEQX*10
       ENCODE(RCDLEN,5040,ITBUF2) OTSPCX,OTSEQX,OTSEQY
 5040 FORMAT(80I1)                                                 00037270
C                                                                  00037280
C                                                                  00037290
C      TRANSFER CARD IMAGE IN ITBUF2 TO OUTPUT BUFFER IN SUBROUTINE BLKWRT.00037290
C                                                                  00037300
       CALL BLKWRT                                                 00037310
C                                                                  00037320
C      CLEAR OTSPC AND INCREMENT OTSEQ.                            00037330
C                                                                  00037340
       DO 90 K=1,26                                                00037350
       OTSPC(K)=0                                                  00037360
       DO 90 M=1,3
   90 OTSPCX(M,K)=0
       OTSEQ=OTSEQ+1                                               00037370
       J=-1                                                        00037380
  100 CONTINUE                                                     00037390
C                                                                  00037400
C      SOME DATA REMAINS IN OTSPC (EVEN IF IT IS END-OF-SCAN ZEROS);  00037410
```

```
C    WRITE IT OUT.                                                    00037420
C                                                                     00037490
      DO 103 M=1,26
      I1=OTSPC(M)
      I2=I1/100
      I3=I1/10-I2*10
      I4=I1-I3*10-I2*100
      OTSPCX(1,M)=I2
      OTSPCX(2,M)=I3
      OTSPCX(3,M)=I4
  103 CONTINUE
      OTSEQX=OTSEQ/10
      OTSEQY=OTSEQ-OTSEQX*10
      ENCODE(RCDLEN,5040,ITBUF2) OTSPCX,OTSEQX,OTSEQY
C                                                                     00037510
C     TRANSFER SCAN RECORD FROM ITBUF2 TO OUTPUT BUFFER.              00037520
C                                                                     00037530
      CALL BLKWRT                                                     00037540
      RETURN                                                          00037550
      ENTRY EPAHDR                                                    00037560
C                                                                     00037570
C     ENTRY POINT TO READ FILE HEADER RECORDS (4) AND TRANSFER TO OUTPUT 00037580
C     BUFFER.                                                         00037590
C                                                                     00037600
C  HERE WE CHECK FOR A PREVIOUS EOF...                               00037610
      IF(EOF.EQ.0)GO TO 105                                           00037620
      EOF=1                                                           00037630
      RETURN                                                          00037640
  105 CONTINUE                                                        00037650
      CALL BLKRD                                                      00037660
      IF (IOERR.LT.0) GO TO 2000                                     00037670
  110 CONTINUE
C                                                                     00037740
      DECODE(RCDLEN,5010,ITBUF1)      NAME,HDRFLG,DATE,RUNHR,RUNMIN   00037750
 5010 FORMAT(3A4,1X,I5,2X,2A4,I3,1X,I2,46X)
C                                                                     00037760
      DO 120 I=1,20                                                   00037770
  120 ITBUF2(I)=ITBUF1(I)                                             00037780
      CALL BLKWRT                                                     00037790
      CALL BLKRD                                                      00037800
      IF (IOERR.LT.0) GO TO 2000                                     00037810
C                                                                     00037880
      DECODE(RCDLEN,5015,ITBUF1) SAMPID,INAM                          00037890
 5015 FORMAT(16A4,10X,A4,A2)
C                                                                     00037900
      DO 130 I=1,20                                                   00037910
  130 ITBUF2(I)=ITBUF1(I)                                             00037920
      CALL BLKWRT                                                     00037930
      CALL BLKRD                                                      00037940
      IF (IOERR.LT.0) GO TO 2000                                     00037950
C                                                                     00038020
      DECODE(RCDLEN,5020,ITBUF1)      RUNCON,SECSCN                   00038030
 5020 FORMAT(16A4,10X,F6.2)
C                                                                     00038040
      DO 140 I=1,20                                                   00038050
  140 ITBUF2(I)=ITBUF1(I)                                             00038060
      CALL BLKWRT                                                     00038070
      CALL BLKRD                                                      00038080
```

```
C            IF (IOERR.LT.0) GO TO 1000                                    00038090
C                                                                          00038160
      5025 FORMAT(6X,2A4,6X,2A4,6X,2A4,6X,5A4,5X,I3,1X,I3)                  00038170
C          DECODE(RCDLEN,5025,ITBUF1)         BUF4,LOPMAS,HIPMAS
C
           DO 150 I=1,20                                                   00038180
       150 ITBUF2(I)=ITBUF1(I)                                             00038190
           CALL BLKWRT                                                     00038200
           RETURN                                                         00038210
C                                                                          00038220
C     END-OF-FILE PROCESSING (IOERR < 0).                                 00038230
C                                                                          00038240
      1000 IF (IOERR.NE.-2) GO TO 2000                                    00038250
           EOF=1                                                          00038260
           CALL BLKWRT                                                    00038270
           CALL NTRAN$(IOUT,9,22)                                         00038280
           WRITE(IPTR1,5030) CNTIN,CNTOUT,EOF                             00038290
      5030 FORMAT(' AT EOF CNTIN =',I6,', CNTOUT =',I6,' EOF = ',I10)      00038300
           RETURN                                                         00038310
C                                                                          00038320
C     ERROR PROCESSING.                                                   00038330
C     IOERR<-2                                                            00038340
C                                                                          00038350
      2000 EOF=-IOERR                                                     00038360
           CALL BLKWRT                                                    00038370
           CALL NTRAN$(IOUT,9,22)
           WRITE(IPTR1,5035) CNTIN, CNTOUT, EOF                           00038380
      5035 FORMAT(' AT ERROR CNTIN =',I6,', CNTOUT =',I6,' EOF = ',I10)    00038390
           RETURN                                                         00038400
           END                                                           00038410
           SUBROUTINE BLKRD                                               00038420
C                                                                          00038430
C     THIS SUBROUTINE TRANSFERS INPUT DATA FROM THE INCOS TAPE OF 128-WORD00038440
C     (512-CHARACTER) BLOCKS INTO A 20-WORD (80-CHARACTER) BUFFER.        00038450
C                                                                          00038460
C     WHEN THE NTRAN BUFFER NO LONGER CONTAINS ENOUGH DATA FOR ONE LOGICAL00038470
C     RECORD (<20 WORDS), THE TAIL OF THE BUFFER IS WRAPPED AROUND TO THE 00038480
C     BEGINNING OF THE BUFFER AND A NEW BLOCK READ INTO THE END OF THE    00038490
C     BUFFER VIA A CALL TO NTRAN$.                                        00038500
C                                                                          00038510
           COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPRT3,IIN,IOUT                 00038520
           COMMON /IOBUF/ ITBUF1,CNTIN,CNTOUT,IOERR,ITBUF2                00038530
           INTEGER*4 ITBUF1(20), CNTIN,CNTOUT,IOERR,ITBUF2(20)           00038540
           INTEGER*4 IISTRT/1/, BLKLEN/128/,RCDLEN/20/,IIEND/0/,         00038550
          * IBUF(148)                                                     00038560
C                                                                          00038570
C     CHECK STARTING POSITION IN BUFFER.  IF IISTRT > (IIEND-RCDLEN+1)    00038580
C     READ A NEW BLOCK.                                                   00038590
C                                                                          00038600
           IF (IISTRT.LE.(IIEND -RCDLEN+1)) GO TO 40                      00038610
           IF (IISTRT.EQ.(IIEND+1)) GO TO 20                              00038620
C                                                                          00038630
C     IF BUFFER HAS INSUFFICIENT DATA TO READ, MOVE RECORD TO BEGINNING OF00038640
C     BUFFER AND STRING A NEW INPUT BLOCK BEHIND IT.                      00038650
C                                                                          00038660
           J=0                                                            00038670
           DO 10 I=IISTRT,IIEND                                           00038680
           J=J+1                                                          00038690
```

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```
      10 IBUF(J)=IBUF(I)                                                  00038700
         IISTRT=J+1                                                       00038710
         GO TO 30                                                         00038720
      20 IISTRT=1                                                         00038730
C                                                                         00038740
C        CALL BLOCK READ SUBROUTINE (SIMULATED FOR IBM 370 TESTING).      00038750
C                                                                         00038760
      30 CALL NTRAN$(IIN,3,BLKLEN,IBUF(IISTRT),IOERR,22)                  00038770
         CNTIN=CNTIN+1                                                    00038780
C                                                                         00038790
C        UPDATE BUFFER LENGTH TO REFLECT NEWLY READ DATA.                 00038800
C                                                                         00038810
         IIEND =IISTRT+BLKLEN-1                                           00038820
         IISTRT=1                                                         00038830
C                                                                         
C        PROCESS NEXT LOGICAL RECORD.                                     
C                                                                         
      40 J=0                                                              00038840
         IEND=IISTRT+19                                                   00038850
         DO 50 I=IISTRT,IEND                                              00038860
         J=J+1                                                            00038870
         ITBUF1(J)=IBUF(I)                                                00038880
      50 CONTINUE                                                         00038890
C        CALL TRACE(IISTRT)                                               00038900
         IISTRT=IEND+1                                                    00038910
         RETURN                                                           00038920
         END                                                             00038930
         SUBROUTINE BLKWRT                                                00038940
C                                                                         00038950
C     THIS SUBROUTINE FILLS A 512-CHARACTER (128-WORD) OUTPUT BUFFER      00038960
C     WITH 80-CHARACTER RECORDS.  WRAPAROUND IS USED TO MAKE THE BUFFER   00038970
C     COMPLETELY FULL AS REQUIRED BY INCOS.  THE BLOCKS, WHEN FULL, ARE   00038980
C     ACTUALLY WRITTEN ON TAPE BY SUBROUTINE NTRAN$.                      00038990
C                                                                         00039000
         COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPRT3,IIN,IOUT                   00039010
         COMMON /FLAGS/EOF                                                00039020
         COMMON /IOBUF/ ITBUF1,CNTIN,CNTOUT,IOERR,ITBUF2                  00039030
         INTEGER*4 ITBUF1(20), CNTIN,CNTOUT,IOERR,ITBUF2(20)             00039040
         INTEGER*4 IBUF(20),        OBUF(148)/148*4H    /,BLKLEN/128/,   00039050
       * RCDLEN/80/,IOSTRT/1/,IBLANK/4H    /,IOEND/20/                    00039060
         EQUIVALENCE (IBUF(1),ITBUF2(1))                                  00039070
C                                                                         00039080
C        CHECK TO SEE WHETHER BUFFER IS ALREADY FULL TO 512 CHARACTERS.   00039090
C                                                                         00039100
C        ALSO, PUT OUT THE LAST BLOCK(S) (THERE MAY BE TWO REQUIRED) AT END- 00039110
C        OF-FILE OR ERROR IN READING OR WRITING.                         00039120
         IF (IOSTRT.GT.128.OR.EOF.NE.0) GO TO 30                         00039140
C                                                                         00039150
C        STORE FILLED TRANSFER BUFFER INTO OUTPUT BUFFER OBUF.            00039160
C                                                                         00039170
      10 IOEND=IOSTRT+19                                                  00039180
         J=0                                                             00039190
         DO 20 I=IOSTRT,IOEND                                            00039210
         J=J+1                                                            00039220
      20 OBUF(I)=IBUF(J)                                                  00039230
         IOSTRT=IOEND+1                                                   00039240
         RETURN                                                          00039250
C                                                                         00039260
```

```
C     UPON ENTERING AND FINDING A FULL BUFFER, WRITE IT TO TAPE.            00039270
C                                                                          00039280
   30 CALL NTRAN$(IOUT,1,BLKLEN,OBUF(1),IOERR,22)                          00039290
   31 CNTOUT=CNTOUT+1                                                       00039310
C                                                                          00039320
C     ADJUST CONTENTS OF OBUF SO THAT IT CONTAINS THE UNWRITTEN PORTION OF 00039330
C     A 80-CHARACTER RECORD.  FILL THE REST OF OBUF WITH BLANKS.           00039340
C                                                                          00039350
   32 IOSTRT=1                                                             00039360
   33 IF (IOEND.LE.128) GO TO 50                                           00039370
   34 J=0                                                                  00039380
      DO 40 I=129,IOEND                                                    00039390
      J=J+1                                                                00039400
   40 OBUF(J)=OBUF(I)                                                      00039410
      IOSTRT=J+1                                                           00039420
      IOEND=J                                                              00039430
C                                                                          00039440
C     STORE BLANKS IN REMAINDER OF OBUF.                                   00039450
C                                                                          00039460
   50 DO 60 I=IOSTRT,148                                                   00039470
   60 OBUF(I)=IBLANK                                                       00039480
C                                                                          00039510
C     GET THE LAST BIT OF DATA ONTO TAPE IF EOF OR ERROR.                  00039520
C                                                                          00039530
      IF (IOEND.LT.IOSTRT.AND.EOF.GT.0) GO TO 30                           00039490
      IF (EOF.EQ.0) GO TO 10                                               00039500
C                                                                          00039540
C     OTHERWISE, FINISHED.                                                 00039550
C                                                                          00039560
      RETURN                                                               00039570
      END
      BLOCK DATA                                                           00039770
      COMMON /FLAGS/ EOF                                                   00039780
      INTEGER*4 EOF/0/                                                     00039790
      COMMON /IOBUF/ ITBUF1,CNTIN,CNTOUT,IOERR,ITBUF2                      00039800
      INTEGER*4 ITBUF1(20),CNTIN,CNTOUT,IOERR,ITBUF2(20)                   00039810
      DATA CNTIN/0/,CNTOUT/0/,ITBUF1/20*4H    /,IOERR/0/,                  00039820
     1ITBUF2/20*4H    /                                                    00039830
      END                                                                  00039840
C THIS SUBROUTINE WAS CALLED ONLY FROM CUEXEC SO                          00000010
C CUEXEC WAS ELIMINATED AND ITS STATEMENTS WERE                          00000020
C INSERTED IN GCMSOL WHICH WAS IN TURN MADE THE MAIN PGM.                00000030
C                                      WM.F. HARGROVE 9/30/77             00000040
C..    SUBROUTINE GCMSOL(CLNFLG)                                         00000050
      INTEGER CLNFLG                                                     00000060
C      THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT      00000070
C      FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND         00000080
C      GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION   00000090
C      (GRANT NGR-05-020-632).                                          00000100
      INTEGER MASBUF(6),VALBUF(6),AJACEN,AHEAD,ISO(1000)                00000110
      INTEGER NAME,RDATE,BITMAP,GCTIME,LIBMAP,INTEG,LOMASS,MAD,ADS      00000120
      INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO            00000130
      INTEGER LSTMIN,SPEC,IND,IR,BK,NM,NTM,PNAME(32)                    00000140
      INTEGER HIST(10),UNIT,NNAME(18),IRNO                              00000150
      INTEGER NUSPEC,NMASS,OVLAP,EXPNAM,SRLIB(5),SECOND                00000160
      INTEGER ODUBLT,QSATS,NLINE,RAWBUF,FSTPGE,FSTREC                   00000170
      INTEGER SATLST,SATINX,PASS1,ITOM,EOF                              00000180
      INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7                  00000190
```

```
      INTEGER*4 TIMREM,TIMCNT                                      00000200
      REAL      SPARE5,SPARE6                                      00000210
      REAL      ISVP8,ISVP9                                        00000220
      REAL      QNORM                                              00000230
      REAL*8    C4,C1,C2,SGX,SHX                                   00000240
      DIMENSION G(9),H(11),GNU(18),HNU(18)                        00000250
      COMMON PKHIST(20),NPHIST(20)                                00000260
      COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5           00000270
      COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                   00000280
      COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                     00000290
      COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                  00000300
      COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT         00000310
      COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                         00000320
      COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS            00000330
      COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)         00000340
      COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7     00000350
      COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                    00000360
      COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX         00000370
      COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5)  00000380
      COMMON /CSATLS/SATLST(25),SATINX                            00000390
      COMMON /CAHEA/AHEAD(5)                                      00000400
      COMMON /PRNTFG/IPFLAG                                       00000410
      COMMON /MODES/ SGMODE(3),SHMODE(3),GMODE,HMODE              00000420
      COMMON /MASSES/ ISGMAS(3),ISHMAS(3),IGMASS,IHMASS           00000430
      COMMON /ERRORS/RMASS,ERRMAX,NERR,SIGERR,SECOND(411)         00000440
      COMMON /IFF/IFLAG(3)                                        00000450
      COMMON /AJACNT/AJACEN(2)                                    00000460
      COMMON /BACKER/SUMG,SUMG2                                   00000470
      COMMON /DUBBER/C4,C1,C2,SGX,SHX                             00000480
      COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                     00000490
      COMMON /HIND/IH1,IH2,MSINGS(2,50),MINX,LINGS(50),LINX       00000500
      COMMON /DUBFLG/IDUB                                         00000510
      COMMON /CRATMX/RATMXX                                       00000520
      COMMON /LFTRIT/ILEFT,IRIGHT                                 00000530
      COMMON /DUBBUG/IDEBUG                                       00000540
      COMMON /MONTOR/MONSPC,MONMAS                                00000550
      COMMON /SLOTNO/NSLOT                                        00000560
      COMMON /CHEMPO/QDUBLT,QNORM,QSATS,NLINE                     00000570
      COMMON /CFSTPG/FSTPGE                                       00000580
      COMMON /CRAWBU/RAWBUF(411)                                  00000590
      COMMON /LSQ/PASS1                                           00000600
      COMMON /CFSTRE/FSTREC                                       00000610
      COMMON /TOMS/ITOM                                           00000620
      COMMON /IMAD/MAD                                            00000630
      COMMON /IADS/ADS                                            00000640
      COMMON /NA/PNAME                                            00000650
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT              00000660
C     IH1,IH2,IFLAG1,IFLAG2 USED IN TLOC AND ITS BRANCHES.       00000670
C HERE CLEANUP HAS BEEN GIVEN THE CAPABILITY OF MULTIPLE RUN     00000680
C PROCESSING - AND THE I/O UNIT NUMBERS HAVE BEEN PUT IN A       00000690
C COMMON BLOCK NAMED /UNITS/                                     00000700
C                                      WM F HARGROVE             00000710
C                                      11/29/78                  00000720
      IRDR=4                                                     00000730
      IPTR1=6                                                    00000740
      IPTR2=6                                                    00000750
      IPTR3=6                                                    00000760
      IIN=7                                                      00000770
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          IOUT=9                                                          00000780
          IRNO=0                                                          00000790
          CALL CUPRNT(3,NPHIST,MASBUF,PKHIST,AVE,                         00000800
         1ERRMAX,ERR2,MODE1,MODE1,MODE2)                                  00000810
C GET CONTROL PARAMETERS - PARDIR HAS BEEN REWRITTEN AS OF               00000820
C                                     12/12/78 WFH - RTI                  00000830
          CALL PARDIR                                                     00000840
C OPEN PRIMARY INPUT AND OUTPUT FILES                                     00000850
          CALL OPNFIL                                                     00000860
C START OF RUN PROCESSING LOOP                                           00000870
   35     IRNO=IRNO+1      .                                              00000880
          EOF=0                                                          00000910
          MU=0                                                           00000920
          IH1 = 1                                                        00000930
          IH2 = 2                                                        00000940
          IFLAG(1) = 0                                                    00000950
          IFLAG(2) = 0                                                    00000960
          TAPCNT = 0                                                      00000970
          AJACEN(2) = 0                                                   00000980
C THIS MOD INSERTED TO HELP WITH UNINITIALIZED G ARRAY                    00000990
C DOWN INSIDE SATLSQ. .....                                              00001000
C                                     RTI WFH 11/21/78                    00001010
          DO 17 I=1,9                                                    00001020
   17     G(I)=0.0                                                        00001030
          DO 10 I = 1,5                                                   00001040
   10     AHEAD(I) = 0                                                    00001050
C THIS MOD INSERTED TO INITIALIZE THE ARRAY GPEAK                        00001060
C INSERTED 11/14/78 - AT RTI BY WFH                                      00001070
          DO 11 I=1,3                                                    00001080
          DO 11 J=1,11                                                    00001090
   11     GPEAK(I,J)=0                                                    00001100
C THIS MOD TO INITIALIZE ARRAY MSINGS...                                 00001110
C INSERTED 4/12/78 - AT RTI BY WFH                                       00001120
          DO 13 I=1,2                                                    00001130
          DO 13 J=1,50                                                    00001140
   13     MSINGS(I,J)=0                                                   00001150
C THIS MOD ALSO TO INITIALIZE AN ARRAY LINGS...                         00001160
C INSERTED 4/13/78 - AT RTI BY WFH                                       00001170
          DO 14 I=1,50                                                    00001180
   14     LINGS(I)=0                                                      00001190
C THESE MODS ARE ALSO TO INITIALIXE ISVN8,ISVN9,ISVP8,ISVP9...           00001200
C INSERTED 4/14//78 - AT RTI BY WFH                                     00001210
          ISVP8=0.0       .                                              00001220
          ISVP9=0.0                                                      00001230
          ISVN8=0                                                        00001240
          ISVN9=0                                                        00001250
C YET ANOTHER MOD TO INITIALIZE THE HISTOGRAMS - NPHIST,PKHIST           00001260
C INSERTED 4/14/78 - AT RTI BY WFH                                       00001270
          DO 15 I=1,20                                                   00001280
          PKHIST(I)=0.0                                                   00001290
   15     NPHIST(I)=0                                                     00001300
C STILL ANOTHER MOD TO INITIALIZE THINGS FOR TLOC - SPARE3 TO SPARE7     00001310
C INSERTED 4/17/78 BY WFH AT RTI                                        00001320
          SPARE3=0                                                       00001330
          SPARE4=0                                                       00001340
          SPARE5=0.0                                                      00001350
          SPARE6=0.0                                                      00001360
C ONCE AGAIN AN UNINITIALIZED VARIABLE - THIS TIME IN LKAHED             00001370
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C MOD INSERTED 4/20/78 AT RTI BY WFH                              00001380
      OVLAP=0                                                      00001390
      DO 12 I = 1,25                                               00001400
 12   SATLST(I) = 0                                                00001410
      SATINX = 1                                                   00001420
C THIS MOD INSERTED TO INITIALIZE ISGMAS FOR A                    00001430
C MOD DOWN INSIDE TLOC TO PREVENT LOOKING FOR                     00001440
C ELUTANTS WHICH HAVE NO SUITABLE MODEL....                       00001450
C                    RTI - BY WFH 5/24/78                          00001460
      DO 16 I=1,3                                                  00001470
      ISHMAS(I)=-1                                                 00001480
 16   ISGMAS(I)=-1                                                 00001490
C     NSLOT,NLINE USED IN KAPUT VIA OUTDAT.                        00001500
      NSLOT = 0                                                    00001510
      NLINE = 0                                                    00001520
      FSTPGE = 1                                                   00001530
      FSTREC = 1                                                   00001540
C     ANOTHER RANDOM VOID .. EH  .. HUI NENG ...                   00001550
      NMASS=411                                                    00001560
      LSTCNT=0                                                     00001570
C HERE THE CALL TO PARDIR HAS BEEN SHIFTED TO THE TOP             00001580
C AND CALLING ARGUMENTS TO SETBUG HAVE BEEN MODIFIED              00001590
C                              WM F HARGROVE                       00001600
C                              11/29/78                            00001610
C     CALL PARDIR(CLNFLG,UNIT,NNAME)                               00001620
      CALL SETBUG(NNAME,EOF)                                       00001630
      IF(EOF.NE.0)GO TO 50                                         00001640
C LOOP CONTROL MODIFIED SO PROGRAM WILL TERMINATE INSIDE MAIN     00001650
C CSECT - WFH RTI 9/31/78                                          00001660
C     MAXSP=MAXSP-10                                               00001670
      NS=13
 40   NS=NS+1
C THE UPDATING OF SPCNO IS NOW DONE INSIDE TLOC                   00001690
C WHERE THE SPECTRUM RECORDS ARE INPUT...                         00001700
C THIS WAS DONE SO THAT SPCNO COULD KEEP UP WITH                  00001710
C GAPS IN THE SCAN NUMBERS...                                     00001720
C                              WFH - RTI 6/15/78                   00001730
C     SPCNO=SPCNO+1                                                00001740
C ALSO AN EOF FLAG WAS ADDED TO ENSURE TERMINATION INSIDE THE     00001750
C MAIN ROUTINE.....                                               00001760
C                              WFH - RTI 9/31/78                   00001770
      CALL TLOC(NS,M1,M2,M3,IFOUND,EOF)                            00001780
      IF(EOF.EQ.1)GO TO 30                                         00001790
C     IFOUND = 0 IF NO SPECTRUM DETECTED.                         00001800
      IF(IFOUND.EQ.0) GO TO 40                                     00001810
      MU=MU+1                                                      00001820
      IF(MU.LE.1000)GO TO 23                                       00001830
      CALL CUPRNT(4,NPHIST,MASBUF,PKHIST,AVE,ERRMAX,               00001840
     1ERR2,SPCNO,MODE2,MODE2)                                      00001850
C     WRITE(IPTR2,24) SPCNO                                        00001860
C  24 FORMAT('-','*** CLEANUP TERMINATING DUE TO TABLE OVERFLOW ***', 00001870
C    1/,1X,'LAST SPECRUM NO. IS ',I5)                             00001880
      STOP 12                                                      00001890
 23   ISO(MU)=SPCNO                                                00001900
 20   CALL LKAHED(NS,M2,M3,OVLAP,G,H)                              00001910
C     OVLAP = 1 IF ELUTANT DETECTED AHEAD.                        00001920
      IF(OVLAP.EQ.0) GO TO 25                                      00001930
      CALL OFFSET(G,H,GNU,HNU,MODE1,MODE2)                         00001940
```

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C HOPEFULLY THE LAST FIX TO CUPRNT IN ORDER TO MAKE          00001950
C WATFIV HAPPY... THE ONLY ARGUMENTS USED IN THIS CALL ARE    00001960
C         MODE1 AND MODE2                                      00001970
C                                   WFH,RTI 4/26/78            00001980
      CALL CUPRNT(1,NPHIST,MASBUF,PKHIST,AVE,ERRMAX,      .    00001990
     1ERR2,MODE1,MODE2,MODE2)                                  00002000
C       ABOVE PRINTS MODE1 AND MODE2                           00002010
25    CONTINUE                                                 00002020
      ISKP=0                                                   00002030
      PASS1 = 0                                                00002040
      NDIS=1                                                   00002050
C       THIS PASS FOR MASSES DETECTED TO LEFT OF DETECTED SPECTRUM   00002060
C       AND NOT RESOLVED                                       00002070
C       IT SHOULD BE NOTED THAT THE DOUBLET RESOLVER IS ONLY RUN ON  00002080
C       PASS 2.                                                00002090
      CALL GETHGT(NS-2,M1,ISKP,OVLAP,NDIS,G,H,GNU,HNU)         00002100
C       THIS PASS FOR MASSES DETECTED AT THE SPECTRUM          00002110
C                              ---                             00002120
      NDIS=2                                                   00002130
      CALL GETHGT(NS-1,M2,ISKP,OVLAP,NDIS,G,H,GNU,HNU)         00002140
      ISKP=1                                                   00002150
      NDIS=3                                                   00002160
C       THIS PASS FOR MASSES DETECTED TO THE RIGHT OF THE SPECTRUM   00002170
      CALL GETHGT(NS,M3,ISKP,OVLAP,NDIS,G,H,GNU,HNU)           00002180
C       PRINT LEAST SQUARE ERROR STUFF IF DOUBLET FOUND        00002190
      IF(OVLAP .EQ. 0)  GO TO 550                              00002200
      IF (IDEBUG .EQ. 0) GO TO 550                             00002210
      AVE = SIGERR/NERR                                        00002220
      ERRMAX = ERRMAX/NERR                                     00002230
      IMASS = RMASS                                            00002240
C HOPEFULLY THE LAST FIX TO CUPRNT IN ORDER TO MAKE            00002250
C C WATFIV HAPPY... THE ONLY ARGUMENTS USED IN THIS CALL ARE   00002260
C       AVE AND ERRMAX                                         00002270
C                                   WFH,RTI 4/26/78            00002280
   .  CALL CUPRNT(2,NPHIST,MASBUF,PKHIST,AVE,ERRMAX,ERR2,      00002290
     1MODE1,MODE2,MODE2)                                       00002300
C             *     *              *      *                     00002310
C       WRITE OUT Q*H(IHSPEC) STUFF                            00002320
      CALL CUPRNT(5,NPHIST,MASBUF,PKHIST,AVE,ERRMAX,           00002330
     1ERR2,SPCNO,MODE2,MODE2)                                  00002340
C       WRITE(IPTR2,900)                                       00002350
C       WRITE(IPTR2,910)                                       00002360
      ICOUNT = 0   .                                           00002370
      DO 600 I = 1,6                                           00002380
      MASBUF(I) = 0                                            00002390
600   VALBUF(I) = 0                                            00002400
      DO 650 I = 1,411                                         00002410
      IMASS = I + 39 - MAD                                     00002420
      IF(SECOND(I) .EQ. 32767) GO TO 650                       00002430
      ICOUNT = ICOUNT + 1                                      00002440
      IF (ICOUNT .LT. 7) GO TO 620                             00002450
C       WRITE(IPTR2,920) (MASBUF(J),VALBUF(J), J = 1,6)        00002460
   .  CALL CUPRNT(6,MASBUF,VALBUF,PKHIST,AVE,ERRMAX,ERR2,      00002470
     1SPCNO,MODE2,MODE2)                                       00002480
      ICOUNT = 1                                               00002490
      DO 610 J = 1,6                                           00002500
      MASBUF(J) = 0                                            00002510
610   VALBUF(J) = 0                                            00002520
```

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620     MASBUF(ICOUNT) = IMASS                                              00002530
        VALBUF(ICOUNT) = SECOND(I)                                          00002540
650     CONTINUE                                                            00002550
        IF ( MASBUF(1) .EQ. C) GO TO 550                                    00002560
C       WRITE(IPTR2,920) (MASBUF(J),VALBUF(J),J=1,6)                        00002570
        CALL CUPRNT(6,MASBUF,VALBUF,PKHIST,AVE,ERRMAX,ERR2,                 00002580
       1SPCNO,MODE2,MODE2)                                                  00002590
C        THE ABOVE EMPTIES THE BUFFER.                                      00002600
550     CALL OUTDAT(SRLIB,NNAME)                                            00002610
        GO TO 40
C THIS MOD INSERTED IN CONJUNCTION WITH THE EOF FLAG ADDITION TO            00002630
C TLOC                                                                      00002640
C                                        WFH - RTI 9/31/78                  00002650
C THE END OF THE CLEANUP MAIN CSECT HAS BEEN MODIFIED                       00002660
C TO HANDLE MULTIPLE RUN PROCESSING.                                        00002670
C                                        WM F HARGROVE                      00002680
C                                          11/29/78                         00002690
C END OF SPECTRUM RUN                                                       00002700
30      CONTINUE                                                            00002710
        CALL CLSRUN(ISQ,MU)                                                 00002740
        GO TO 35                                                            00002750
C END OF FILE AND TERMINATION OF CLEANUP PROGRAM                            00002760
50      CALL CUPRNT(8,NNAME,VAIBUF,PKHIST,AVE,ERRMAX,                       00002770
       2ERR2,TIMCNT,MODE2,MODE2)                                            00002780
        CALL CLSFIL                                                         00002790
        STOP                                                                00002800
        END                                                                 00002810
        SUBROUTINE BACLSQ(PKHGT)                                            00002820
C                                                                           00002830
C                                                                           00002840
C          THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT     00002840
C          FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND        00002850
C          GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  00002860
C          (GRANT NGR-05-020-632).                                          00002870
C                                                                           00002880
C                                                                           00002890
C          *** THIS ROUTINE USES A MODEL PEAK AND CURRENT PEAK              00002900
C          *** AND DOES A LEAST SQUARES TO COMPUTE THE                      00002910
C          *** BACKGROUND AT PEAK CENTRE (ASSUMES LINEAR BACKGROUND).       00002920
C                                                                           00002930
        INTEGER PKHGT,PASS1                                                 00002940
        COMMON PKHIST(20),NPHIST(20)                                        00002950
        COMMON YM5,Y(9),YP5                                                 00002960
        COMMON G(9)                                                         00002970
        COMMON /LSQ/PASS1                                                   00002980
        COMMON /BACKER/SG,SG2                                               00002990
        REAL    P,C                                                         00003000
C                                                                           00003010
C          *** SOLUTION OF THREE LINEAR EQUATIONS.                          00003020
C                                                                           00003030
C                                                                           00003040
C          P * SG**2 + C  = SGY                                             00003050
C                                                                           00003060
C          P * SG    + C  = SY                                              00003070
C                                                                           00003080
C                                                                           00003090
C             WHICH RESULT FROM THE LEAST SQUARE FITTING OF THE             00003100
C             ERROR TERMS.                                                  00003110
C                                                                           00003120
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C           E(I) = P * G(I) + C - Y(I)        , I = 1,9                    00003130
C                                                                          00003140
C       WE SOLVE FOR P AND SET PEAKHGT = P * GTOP.                         00003150
C                                                                          00003160
C           WHERE GTOP IS THE INTERPOLATED VALUE AT THE SPECTRUMS HISTOGRAM00003170
C       POSITION.                                                          00003180
C                                                                          00003190
        IF( PASS1 .EQ. 1 ) GO TO 10                                        00003200
        PASS1 = 1                                                          00003210
        SG = 0                                                             00003220
        SG2 = 0                                                            00003230
        DO 5 I = 1,9                                                       00003240
        SG = SG + G(I)/9                                                   00003250
5       SG2 = SG2 + G(I) * G(I)/9                                          00003260
10      CONTINUE                                                           00003270
        SY = 0                                                             00003280
        SYG = 0                                                            00003290
        DO 20 I = 1,9                                                      00003300
        SY = SY + Y(I)/9                                                   00003310
20      SYG = SYG + Y(I) * G(I)/9                                          00003320
        P = ( SYG - SY * SG )/( SG2 - SG * SG )                            00003330
        PKHGT = P * G(5)                                                   00003340
C       C = SY - P * SG                                                    00003350
        RETURN                                                             00003360
        END                                                               00003370
        SUBROUTINE BLEED(Y,RATIO)                                          00003380
C       LEAST SQUARE FITS A LINE TO DATA TO DETERMINE ITS LINEARITY.       00003390
        REAL AVY,AXY,AXX,X,B,M,RATIO                                       00003400
        INTEGER N,I                                                        00003410
        REAL Y(7),ERROR,FIT(7)                                            00003420
        AVY = 0                                                            00003430
        AXY = 0                                                            00003440
        AXX = 0                                                            00003450
        DO 200 I = 1,7                                                     00003460
        X = I - 4                                                          00003470
        AVY = AVY + Y(I)                                                   00003480
        AXY = AXY + X * Y(I)                                               00003490
200     AXX = AXX + X*X                                                    00003500
        AVY = AVY/7                                                        00003510
        AXX = AXX/7                                                        00003520
        AXY = AXY/7                                                        00003530
        B = AVY                                                            00003540
        M = AXY/AXX                                                        00003550
C       Y = M X  + B                                                       00003560
C                                                                          00003570
C                                                                          00003580
C THE ERROR RATIO CALCULATION HAS BEEN MODIFIED SUBSTANTIALLY              00003590
C BECAUSE IT WAS FOUND TO BE HAYWIRE IN THE PREVIOUS VERSION.              00003600
C THE MOD IS A JOINT EFFORT OF DR/SHAH/PC/WFH                              00003610
C                               ENTERED BY WFH-RTI 9/31/78                 00003620
C                                                                          00003630
        IF(AVY.EQ.0)GO TO 400                                             00003640
        RMS=0.0                                                            00003650
        DO 300 I=1,7                                                       00003660
        FIT(I)=M*(I-4)+B                                                   00003670
        ERROR=FIT(I)-Y(I)                                                  00003680
300     RMS=RMS+ERROR*ERROR                                               00003690
        RMS=SQRT(RMS)/7.0                                                  00003700
        RATIO=RMS/AVY
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        RETURN                                                      00003710
C                                                                   00003720
  400 RATIO=0.0                                                     00003730
        RETURN                                      ,               00003740
        END                                                         00003750
C     THIS SUBROUTINE DOES ALL PRINTING                             00003760
C     FOR CLEANUP. PLEASE USE IT TO ADD NEW PRINTING                00003770
C     IN ANY SUBROUTINE.                          .                 00003780
C                                                                   00003790
C     THE CALL STATEMENT ALLOWS FOR PASSING OF ARRAYS               00003800
C     REALS AND INTEGERS.                                           00003810
C                                                                   00003820
C                                                                   00003830
C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT  00003840
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND     00003850
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00003860
C     (GRANT NGR-05-020-632).                                       00003870
C                                                                   00003880
        SUBROUTINE CUPRNT(N,IAR,IAR2,AR,R1,R2,R3,I1,I2,I3)          00003890
        INTEGER N,I1,I2,I3,IONE,NINE                                00003900
        REAL R1,R2,R3                                               00003910
C THE DIMMENSIONS OF IAR AND AR HAVE BEEN CHANGED TO SUIT WATFIV    00003920
C THEY WERE AT 9....MUCH OF THIS CODE SEEMS NONSENSE...             00003930
C                                         WFH RTI 26/4/78           00003940
        DIMENSION IAR(1),AR(1),IAR2(1)                              00003950
        COMMON /DUBBUG/IFLAG                                        00003960
        COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT              00003970
        DATA IONE,NINE/1,9/                                         00003980
C                                                                   00003990
C     IFLAG IS RESET IF NO PRINTING IS TO BE DONE/                  00004000
C                                                                   00004010
C     IF (IFLAG.EQ.0) RETURN                                        00004020
        GO TO (10,140,150,160,170,180,200,210),N                    00004030
C            .                                                      00004040
C     THE ABOVE IS A CASE STATEMENT FOR EXECUTING PRINT             00004050
C     OPTIONS.C                                                     00004060
C                                                                   00004070
C     GCMSOL RPINTING OF MODE1,MODE2                                00004080
   10 IF(IFLAG.EQ.0)RETURN                                          00004090
        WRITE(IPTR2,510) I1,I2                                      00004100
        RETURN                                                      00004110
C                                                                   00004120
  140 IF(IFLAG.EQ.0)RETURN                                          00004130
        WRITE(IPTR2,1400) R1,R2                                     00004140
        RETURN                                                      00004150
C     FORMAT STATEMENTS FOLLOW.                                     00004160
C                                                                   00004170
  510 FORMAT(/1X,'    HISTOGRAM LOCATIONS OF THE TWO SPECTRA ARE:'/ 00004180
       -8X,'G-POSITION = ',I2,2X,'H-POSITION = ',I4)                00004190
 1400 FORMAT(/' LEAST SQUARES ERROR STUFF FOR DUBLET:'/             00004200
       -'     AVE. ERR.          AVE RMS ERR'                       00004210
       -,/,1X,E15.8,4X,E15.8,//)                                    00004220
C THESE PRINT STATEMENTS HAVE BEEN ADDED AS PART OF THE             00004230
C GENERAL REVAMPING OF CUPRNT....    WFH RTI 9/31/78                00004240
C           .                                                       00004250
  150 WRITE(IPTR2,101)                                     `.       00004260
  101 FORMAT('-','START OF CONVERTED MASS SPEC CLEANUP PROGRAM')     00004270
        RETURN                                                      00004280
```

```
C                                                                    00004290
  160 WRITE(IPTR2,24) I1                                             00004300
   24 FORMAT('-','*** CLEANUP TERMINATING DUE TO TABLE OVERFLOW ***',00004310
     1/,1X,'LAST SPECTRUM NO. IS ',I5)                               00004320
      RETURN                                                         00004330
C                                                                    00004340
  170 IF(IFLAG.EQ.0)RETURN                                           00004350
      WRITE(IPTR2,900)                                               00004360
  900 FORMAT(//,20X,' COMPUTED H(MODE) * Q',/)                       00004370
      WRITE(IPTR2,910)                                               00004380
  910 FORMAT(' MASS,VALUE   MASS VALUE   MASS VALUE   MASS VALUE   MASS VAL00004390
     *UE  MASS VALUE'/)                                              00004400
      RETURN                                                         00004410
C                                                                    00004420
C                                                                    00004430
  180 IF(IFLAG.EQ.0)RETURN                                           00004440
      WRITE(IPTR2,920) (IAR(I),IAR2(I),I=1,6)                        00004450
  920 FORMAT(6(3X,I3,1X,I5))                                         00004460
      RETURN                                                         00004470
C CUPRNT STATEMENTS 7 AND 8 HAVE BEEN MODIFIED TO                    00004480
C FIT IN WITH THE SCHEME OF MULTIPLE RUN PROCESSING.                 00004490
C                                      WM F HARGROVE                 00004500
C                                       11/29/78 RTI                 00004510
  200 WRITE(IPTR2,11)    I2,(IAR(I),I=1,18)                          00004520
   11 FORMAT(1X,'END OF PROCESSING FOR RUN #',I2,                    00004530
     2' RUN TITLE: ',18A4)                                           00004550
      RETURN                                                         00004560
C                                                                    00004570
  210 WRITE(IPTR2,102)                                               00004580
  102 FORMAT('-','***END OF CLEANUP PROCESSING***')                  00004590
      RETURN                                                         00004600
      END                                                            00004610
      SUBROUTINE DETEKT (PKHIST,NPHIST,DTFLAG,NLWCUT,NUPCUT          00004620
     &    ,NL,NU,IDXL,IDXU,INDX)                                     00004630
C                                                                    00004640
C        THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT00004650
C        FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND   00004660
C        GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION00004670
C        (GRANT NGR-05-020-632).                                    00004680
C                                                                    00004690
      INTEGER PLIMIT,DTFLAG,CPLMIT,SVFLAG,CASEI                      00004700
      REAL MX,MX2,INTSUM                                             00004710
      DIMENSION PKHIST(20),NPHIST(20)                                00004720
      COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                        00004730
C     MINNY IS USED FOR FEWER THAN 5 PEAKS                           00004740
C     REQUIRE  TOTAL ION CURRENT FOR DETECTED SPECTRUM TO BE MINTIC  00004750
C     IN AND AROUND THE MAX IF 5 PEAKS LOCALLY.                      00004760
      COMMON /TOMS/ITOM                                              00004770
      COMMON /CAHEA/AHEAD(5)                                         00004780
      INTEGER AHEAD,ITOM                                             00004790
C     **************************************************             00004800
C     WE SCAN THE HISTOGRAMIC WINDOW +NL,NU@ FOR A MAXIMUM           00004810
      DTFLAG=0      .                                                00004820
      INDX=NL                                                        00004830
      NUM=NPHIST(NL)                                                 00004840
      MX=PKHIST(NL)                                                  00004850
C     THE HISTOGRAMIC WINDOW +IDXL,IDXU@ IS WHERE A MAXIMUM          00004860
C     WILL OCCUR IF A SPECTRUM IS ELUTING.                           00004870
```

```
          NUM2=NPHIST(IDXL)                                        00004880
          MX2=PKHIST(IDXL)                                         00004890
          INDX2=IDXL                                               00004900
C             MX,NUM = MAX +NL,NU@  &   MX2,NUM2 = MAX +IDXL,IDXU@ 00004910
          DO 10 I=NL,NU                                            00004920
          IF ( MX .GE. PKHIST(I) ) GO TO 9                         00004930
          MX=PKHIST(I)                                             00004940
          NUM=NPHIST(I)                                            00004950
          INDX=I                                                   00004960
9         CONTINUE                                                 00004970
C         NOTE: +IDXL,IDXU@ IS  WINDOW FOR DETECTING ELUTANT NOW   00004980
          IF ( I .LE. IDXL .OR.  I .GT. IDXU ) GO TO 10            00004990
          IF ( MX2 .GE.  PKHIST(I) ) GO TO 10                      00005000
C         GET MAXIMUM IN WINDOW  + IDXL,IDXU @                     00005010
          MX2=PKHIST(I)                                            00005020
          NUM2=NPHIST(I)                                           00005030
          INDX2=I                                                  00005040
10        CONTINUE                                                 00005050
C         SEE IF IN RIGHT HISTOGRAM WINDOW, +IDXL,IDXU@            00005060
          IF ( INDX .GE. IDXL .AND.  INDX .LE. IDXU ) GO TO 15     00005070
C         IF WE GET HERE THE ABSOLUTE MAXIMUM WAS NOT IN +IDXL,IDXU@ 00005080
C         AND  IDXL  .LE.  INDX2   .LE. IDXU                       00005090
C         REQUIRE: 1. THAT TIC (INDX2) BE LARGER THAN ITS IMMEDIATE 00005100
C                     NEIGHBORS.                                   00005110
C                  2. THAT PKHIST(IDXU) + PKHIST(IDXU+1)           00005120
C                     + PKHIST(IDXL)    .GE.    MINTIC.            00005130
          IF ( MX2 .LT. PKHIST(INDX2-1) ) RETURN                  00005140
          IF ( MX2 .LT. PKHIST(INDX2+1) ) RETURN                  00005150
C         CHECK ON HOW CLOSE WE WILL ALLOW HISTOGRAM BUMPS.        00005160
C         DEFAULTS TO 2 SLOTS APART. SPECIAL FLAG ITOM IS          00005170
C         USED FOR FRAGMENTOGRAPHY RUNS TO TRY TO SEPARATE         00005180
C         DEUTERATED PEAKS FROM NON-DEUTERATED PEAKS.              00005190
C                                                                  00005200
C THIS IS A TEMPORARY MOD IN ORDER TO GATHER STATISTICS ON         00005210
C THE INPUT PARAMETER ITOM - CODE 6                                00005220
C                                         WFH RTI 9/31/78          00005230
C                                                                  00005240
C         ISPC=0                                                   00005250
C         ITYP=6                                                   00005260
C         WRITE(20,6251) ITYP,ISPC                                 00005270
C6251 FORMAT(A4,A4)                                                00005280
C                                                                  00005290
          IF ( ITOM .EQ.  1 ) GO TO 79                             00005300
          IF ( MX2 .LT.  PKHIST(INDX2-2) ) RETURN                 00005310
          IF ( MX2 .LT.  PKHIST(INDX2+2) ) RETURN                 00005320
C                                                                  00005330
C TEMPORARY MOD IN ORDER TO GATHER STATISTICS ON                   00005340
C THE INPUT PARAMETER ITOM - CODE 7                                00005350
C                                         WFH RTI 9/31/78          00005360
C         ISPC=0                                                   00005370
C         ITYP=7                                                   00005380
C         WRITE(20,6254) ITYP,ISPC                                 00005390
C6254 FORMAT(A4,A4)  ,                                             00005400
79        CONTINUE                                                 00005410
          PKSUM = PKHIST(IDXL) + PKHIST(IDXL+1) + PKHIST(IDXU)     00005420
          IF ( IDXL .NE. 4 ) GO TO 12                              00005430
          IF ( AHEAD(1) .EQ. 1 ) PKSUM = MINTIC                    00005440
C         THE ABOVE GUARANTEES DETECTION IF SPECTRUM WAS DETECTED  00005450
```

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C        AHEAD.                                                   00005460
12       CONTINUE                                                 00005470
C                                                                 00005480
C THIS IS A TEMPORARY MOD IN ORDER TO GATHER STATISTICS ON        00005490
C THE INPUT PARAMETER ITOM - CODE 5                               00005500
C                                    WFH RTI 9/31/78              00005510
C        ISPC=0                                                   00005520
C        ITYP=5                                                   00005530
C        WRITE(20,6252) ITYP,ISPC,PKSUM                           00005540
C6252 FORMAT(A4,A4,36X,A4)                                        00005550
         IF ( PKSUM .LT. MINTIC ) RETURN                          00005560
         NLWCUT=INDX2-2                                           00005570
         NUPCUT=INDX2+2                                           00005580
         INDX=INDX2                                               00005590
C        DTFLAG = 1 SAYS WE'VE FOUND ONE                          00005600
         DTFLAG=1                                                 00005610
         RETURN                                                   00005620
15       CONTINUE                                                 00005630
C        WE NOW SUM NUMBER OF PEAKS AND TIC.                      00005640
         IF ( IDXL .LT. 7 ) GO TO 16                              00005650
C        MAKE SURE WE HAVE A HISTOGRAMIC BUBBLE                   00005660
C        IF LOOKING AHEAD.                                        00005670
         BUBBLE = PKHIST(INDX)                                    00005680
         IF ( BUBBLE .LT. PKHIST(INDX-1) ) RETURN                 00005690
         IF ( BUBBLE .LT. PKHIST(INDX-2) ) RETURN                 00005700
16       CONTINUE                                                 00005710
         PKSUM = NPHIST(IDXL)                                     00005720
         INTSUM = PKHIST(IDXL)                                    00005730
C        IF IDXL = 9 THEN WE ARE LOOKING AHEAD, AND AN EARLIER    00005740
C        ELUTANT WAS DETECTED AT 6. WE ONLY SCANNED ↑9,10@.       00005750
         IF (IDXL .EQ. 9) GO TO 150                               00005760
         PKSUM = PKSUM + NPHIST(IDXL + 1)                         00005770
         INTSUM = INTSUM + PKHIST(IDXL + 1)                       00005780
         IF ( IDXL .EQ. 8 ) GO TO 100                             00005790
C        HERE WE ONLY SCANNED ↑8,10@                              00005800
         PKSUM = PKSUM + NPHIST(IDXU)                             00005810
         INTSUM = INTSUM + PKHIST(IDXU)                           00005820
         IF ( IDXL .EQ. 7 ) GO TO 100                             00005830
C        HERE WE SCANNED ↑7,10@. IN ALL SPECIAL CASES A ELUTANT WAS 00005840
C        DETECTED IN ↑4,5,6@ SO WE DO NO LEFT BOUNDARY CHECKING.  00005850
C        SEE IF MAXIMUM OCCURRED ON LEFT BOUNDARY                 00005860
         IF ( INDX .NE. IDXL ) GO TO 100                          00005870
         PKSUM = PKSUM + NPHIST(IDXL-1)                           00005880
         INTSUM = INTSUM + PKHIST(IDXL-1)                         00005890
         GO TO 150                                                00005900
C        SEE IF MAXIMUM OCCURRED ON RIGHT BOUNDARY                00005910
100      CONTINUE                                                 00005920
         IF ( INDX .NE. IDXU ) GO TO 150                          00005930
         PKSUM = PKSUM + NPHIST(IDXU+1)                           00005940
         INTSUM = INTSUM + PKHIST(IDXU+1)                         00005950
150      CONTINUE                                                 00005960
C        GUARANTEE SPECTRUM DETECTION IF DETECTED AHEAD.          00005970
         IF ( IDXL .NE. 4 ) GO TO 155                             00005980
         IF ( AHEAD(1) .EQ. 0 ) GO TO 155                         00005990
         PKSUM = MINTIC                                           00006000
         IF ( PKSUM .LT. MINNY ) PKSUM = MINNY                    00006010
155      CONTINUE                                                 00006020
C        CHECK FOR FEWER THAN 5 PEAKS.                            00006030
```

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C                                                                          00006040
C THIS IS A TEMPORARY MOD IN ORDER TO GATHER STATISTICS ON                 00006050
C THE INPUT PARAMETER ITOM - CODE 4                                        00006060
C                                              WFH RTI 9/31/78             00006070
C          ISPC=0                                                          00006080
C          ITYP=4                                                          00006090
C          WRITE(20,6257) ITYP,ISPC,PKSUM,INTSUM                           00006100
C6257 FORMAT(A4,A4,28X,A4,A4)                                              00006110
          IF (PKSUM .GE. 5) GO TO 200                                      00006120
          IF( INTSUM .GE. MINNY ) GO TO 18                                 00006130
          RETURN                                                           00006140
200       CONTINUE          .                                             00006150
C          IF AT LEAST 5 PEAKS, THEN REQUIRE INTSUM > MINTIC.              00006160
          IF(INTSUM .LT. MINTIC) RETURN                                   00006170
18        CONTINUE                                                         00006180
          DTFLAG=1                                                         00006190
          IF ( NL .NE. 1 ) RETURN                                          00006200
C          NL = 1  --> WE ARE NOT LOOKING AHEAD, AND NEED HISTOGRAMIC      00006210
C          BOUNDS, NLWCUT AND NUPCUT.                                      00006220
          SLEFT=0.0                                                        00006230
          SRIGHT=0.0                                                       00006240
          NUM1=INDX+1                                                      00006250
          NUM3=INDX+3                                                      00006260
C          GET HISTOGRAMIC "WEIGHTS" TO THE LEFT AND RIGHT OF THE          00006270
C          MAXIMUM AT PKHIST(INDX).                                        00006280
          J = 0                                                            00006290
          DO 20 I=NUM1,NUM3                                                00006300
          J = J + 1                                                        00006310
          JJ = INDX - J                                                    00006320
          SLEFT = SLEFT + PKHIST(JJ)                                       00006330
          SRIGHT - SRIGHT + PKHIST(I)                                      00006340
20        CONTINUE                                                         00006350
          NLWCUT = INDX - 2                                                00006360
          NUPCUT = INDX + 2                                                00006370
          IF ( SLEFT - SRIGHT ) 30,40,50                                   00006380
C          MORE "WEIGHT" TO RIGHT IF WE GET HERE                           00006390
30        NUPCUT = NUPCUT + 1                                              00006400
          GO TO 40                                                         00006410
C          MORE "WEIGHT" TO LEFT IF WE GET HERE                            00006420
50        NLWCUT = NLWCUT - 1                                              00006430
40        RETURN                                                           00006440
          END                                                              00006450
          SUBROUTINE DUBLET (G,H,Y,STORE,M,IHSPEC,GHGT,ISWD,NS)            00006460
          REAL  GHGT                                                       00006470
          INTEGER STORE,M,IHSPEC,ISWD,SECOND,NS,MAD                        00006480
          REAL KK ,LL,MM,NN                                                00006490
          COMMON /DUBBER/C4,C1,C2,SG,SH                                    00006500
          COMMON /MONTOR/MONSPC,MONMAS                                     00006510
          COMMON /ERRORS/RMASS,ERRMAX,NERR,SIGERR,SECOND(411)             00006520
          COMMON /IMAD/MAD                                                 00006530
          COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                   00006540
          INTEGER 132766      .                                           00006550
          REAL*3    C4,C1,C2,SG,SH                                         00006560
          REAL*8    SY,SGY,SHY,SG2,SH2,SGH                                 00006570
          REAL  .    ERR,ERRM                                              00006580
C          *** ROUTINE TO RESOLVE A DUBLET USING TWO MODEL                 00006590
C          *** PEAKS BY A LEAST SQUARES METHOD. THE MODEL                  00006600
C          *** INCLUDES A LINEAR BACKGROUND.                               00006610
```

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```fortran
C       THE LEAST SQUARE NORMAL EQUATIONS ARE DERIVED FROM         00006620
C       THE FOLLOWING EQUATION FOR ERROR MINIMAZATION:             00006630
C          E(I) = P * G(I) + Q * H ( I ) + C - Y(I)  ,I = 1.14     00006640
C          <X> = AVERAGE VALUE OF X                                00006650
C       THIS LEADS TO THE FOLLOWING SYSTEM OF EQUATIONS :          00006660
C          P * <SG**2> + Q * <SGH>   + C * <SG> = <SGY>            00006670
C          P * <SGH>   + Q * <SH**2> + C * <SH> = <SHY>            00006680
C          P * <SG>    + Q * <SH>    + C        = <SY>             00006690
        REAL    G(18),H(18),Y(18)                                  00006700
        REAL    ERRT1(14),FIT(14)                                  00006710
        REAL    P,Q,C,ZERO,HMD(14),GMD(14)                         00006720
        INTEGER ILOW,IUP                                           00006730
        DATA ZERO/0.0/                                             00006740
        DATA 132766/32760/                                         00006750
C       ***************************HI THERE********************    00006760
C       INITIALIZE SOME VARIABLES                                 00006770
        ILOW = 3                                                   00006780
        IUP = 11                                                   00006790
C       WE TRUNCATE THE SECOND MODEL AT THE 11TH POSITION SO AS    00006800
C       ONLY TO USE POINT WHERE REAL DATA WAS SUPPLIED.           00006810
        AN = IUP - ILOW + 1                                        00006820
C        TEST TO SEE IF WE'VE ALREADY BEEN BY FOR THIS SPECTRUM    00006830
        IF( ISWD . EQ.  0) GO TO 20                                00006840
        ISWD = 0                                                   00006850
        SG2 = 0                                                    00006860
        SGH = 0                                                    00006870
        SG  = 0                                                    00006880
        SH2 = 0                                                    00006890
        SH  = 0                                                    00006900
C       DO SOME          SUMS.                                     00006910
        DO 10 I = ILOW,IUP                                         00006920
        SG = SG + G(I)                                             00006930
        SG2 = SG2 + G(I) * G(I)                                    00006940
        SH = SH + H(I)                                             00006950
        SH2 = SH2 + H(I) * H(I)                                    00006960
        SGH = SGH + G(I) * H(I)                                    00006970
10      CONTINUE                                                   00006980
C        MAKE ALL AVERAGE VALUES                                   00006990
        SG = SG/AN                                                 00007000
        SG2 = SG2/AN                                               00007010
        SH = SH/AN                                                 00007020
        SH2 = SH2/AN                                               00007030
        SGH = SGH/AN                                               00007040
C        NOW DO WHAT COMPUTING WE CAN FOR MODEL STUFF              00007050
        C4  = SG2 - SG * SG                                        00007060
        C1  = SGH - SG * SH                                        00007070
        C2  = SH2 - SH * SH                                        00007080
20      CONTINUE                                                   00007090
        SY=0                                                       00007100
        SGY=0                                                      00007110
        SHY=0                                                      00007120
        DO 30 I = ILOW,IUP                                         00007130
        SY=SY + Y(I)                                               00007140
        SGY=SGY + G(I) * Y(I)                                      00007150
        SHY=SHY + H(I) * Y(I)                                      00007160
30      CONTINUE                                                   00007170
        SY = SY/AN                                                 00007180
        SGY = SGY/AN                                               00007190
```

```
                SHY = SHY/AN
      C         NOW SOLVE FOR P,Q,C                                  00007200
                C5   = SGY - SY * SG                                 00007210
                C3   = SHY - SY * SH                                 00007220
                P = ( C5 * C2 - C3 * C1 )/( C4 * C2 - C1 * C1 )      00007230
                Q = ( C3 - P * C1 )/C2                               00007240
                C = SY - P * SG - Q * SH                             00007250
                GHGT = P * G(7)                                      00007260
                HHGT = Q * H(IHSPEC)                                 00007270
                IF( GHGT .LT. ZERO ) GHGT = ZERO                     00007280
                IF( HHGT .LT. ZERO ) HHGT = ZERO                     00007290
      C         DO MEAN SQUARE ERROR CALCULATION                     00007300
                ERR = 0                                              00007310
                ERRM = 0                                             00007320
                DO 40 I = ILOW,IUP                                   00007330
                GMD(I)    = P * G(I)                                 00007340
                HMD(I)    = Q * H(I)                                 00007350
                FIT(I)    = GMD(I) + HMD(I) + C                      00007360
                ERRT1(I) = Y(I) - FIT(I)                             00007370
                ERRM      = ERRM + ERRT1(I)                          00007380
      40        ERR       = ERR  + ERRT1(I) * ERRT1(I)               00007390
                ERRM = ERRM/AN                                       00007400
                RMS = ERR/AN - ERRM * ERRM                           00007410
                IF( RMS .LT. 0 ) RMS = 0                             00007420
                ERR = SQRT(RMS)                                      00007430
                SIGERR = SIGERR + ERRM                               00007440
                ERRMAX = ERRMAX + ERR                                00007450
                NERR = NERR + 1                                      00007460
                STORE = 1                                            00007470
      C         FLAG FOR SETGHY TO SIGNAL STORING OF NEW VALUE IN NUSPEC(M)  00007480
                IF(HHGT .GT. 132766) HHGT = 132766                  00007490
                SECOND(M) = HHGT                                     00007500
      200       CONTINUE                                            00007510
                RETURN                                              00007520
      C THIS SECTION OF DUBLET DEALS WITH PRINTING                  00007530
      C OUT OF MONITORED SPECTRA AND MONITORED MASSES               00007540
      C IT WAS COMMENTED OUT BECAUSE NO EASY WAY OF                 00007550
      C INCORPORATING THIS DIAGONISTIC INTO THE                     00007560
      C MULTIPLE RUN PROCESSING SCHEME COULD                        00007570
      C BE THOUGHT OF. IT MAY BE REINSTITUTED IN THE                00007580
      C EVENT OF SUBTILE DOUBLET RESOLUTION PROBLEMS.               00007590
      C                              WM F HARGROVE                   00007600
      C                              12/7/78 - RTI                   00007610
      C         IF ( MONMAS .EQ. 0 ) RETURN                          00007620
      C         IM = M + 39-MAD                                      00007630
      C         IS = NS - 6                                          00007640
      C         IF ( MONMAS .NE. IM   .OR. MONSPC .NE. IS) RETURN    00007650
      C         WRITE(IPTR2,2500) ERR,ERRM                          00007660
      C         WRITE(IPTR2,2000) IM,P,Q,C                          00007670
      C         WRITE(IPTR2,2100) (Y(I),I = 3 , 11)                 00007680
      C         WRITE(IPTR2,2200) (G(I),I = 3 , 11)                 00007690
      C         WRITE(IPTR2,2300) (H(I),I = 3 , 11)                 00007700
      C         BAK = C                                              00007710
      C         SQHT = GHGT + Q * H(7) + BAK                         00007720
      C         WRITE(IPTR2,2400) GHGT,BAK,SQHT                     00007730
      C999       RETURN                                             00007740
      C2000 FORMAT(//,' DOUBLET STUFF FOR MASS = ',I3,/             00007750
      C      -,'       P              Q              C        ',/   00007760
                                                                    00007770
```

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C     -.3(2X,F10.3))                                              00007780
C2100 FORMAT(//.' Y-VALUES'.//.5(2X,F7.0).//.4(2X,F7.0))          00007790
C2200 FORMAT(//.' G-VALUES'.//.5(2X,F7.4).//.4(2X,F7.4))          00007800
C2300 FORMAT(//.' H-VALUES'.//.5(2X,F7.4).//.4(2X,F7.4))          00007810
C2400 FORMAT(//.'   P * G(7)   BACK GROUND  P*G + Q*H + C '.      00007820
C     -/.3(4X,F8.0)/)                                             00007830
C2500 FORMAT(//.' RMS ERROR = '.E14.8.' MEAN ERROR = '.E20.8)     00007840
      END                                                         00007850
      SUBROUTINE GETHGT(NS.MN.ISKP.OVLAP.NDIS.G.H.GNU.HNU)        00007860
      INTEGER PKHGT.MNB.MI.MN.ISKP.JMPK.NUHGT                     00007870
      DIMENSION G(9).H(11).GNU(18).HNU(18)                        00007880
C     *** THIS ROUTINE IS THE MAIN PROCESSING ROUTINE. IT        00007890
C     *** PICKS UP THE MASS INDICES THAT HAVE BEEN FLAGGED        00007900
C     *** IN THE DETECTION PHASE AND PROCEEDS TO  HANDLE          00007910
C     *** BACKGROUND REMOVAL AND DOUBLET RESOLUTION AND           00007920
C     *** THE PROCESSING OF SATURATED PEAKS. IT IS CALLED         00007930
C     *** THREE TIMES IN PROCESSING ANY ONE COMPONENT DUE TO      00007940
C     *** THE SPREAD THAT CAN EXIST IN PEAK MODES FOR ANY         00007950
C     *** COMPONENT (PARTICULARLY THE LOW INTENSITY ONES).        00007960
      INTEGER NAME.RDATE.BITMAP.GCTIME.LIBMAP.INTEG.LOMASS         00007970
      INTEGER HIMASS.POINTS.TAPCNT.MAXSP.LSTCNT.DEVICE.SPCNO       00007980
      INTEGER SPEC.IND.IR.BK.NM.NTM                                00007990
      INTEGER GPEAK.SPARE1.SPARE2.SPARE3.SPARE4.SPARE7             00008000
      INTEGER ISWD.MAD                                             00008010
      INTEGER NUSPEC.NMASS.OVLAP                                   00008020
      INTEGER SECOND                                               00008030
      INTEGER PASS1                                                00008040
      INTEGER QDUBLT.QSATS.NLINE.BEDROK.AJACEN.SATLST.SATINX       00008050
      REAL    ISVP8.ISVP9                                          00008060
      REAL HIST(10).YVAL                                           00008070
      REAL    SPARE5.SPARE6                                        00008080
      REAL    QNORM.RATIO                                          00008090
      REAL    PEPCNT                                               00008100
      REAL*8 GTHT                                                  00008110
      COMMON PKHIST(20).NPHIST(20)                                 00008120
      COMMON YVAL(11)                                             00008130
      COMMON GM4.GM3.GM2.GM1.G0.GP1.GP2.GP3.GP4                    00008140
      COMMON SG.SG2.SIG.SI.SI2.AN.AA.BB.CC.DD                      00008150
      COMMON NAME(32).RDATE(5).BITMAP(64).GCTIME                   00008160
      COMMON LIBMAP(17).INTEG.LOMASS.HIMASS.POINTS.TAPCNT          00008170
      COMMON MAXSP.LSTCNT.DEVICE(5).SPCNO                          00008180
      COMMON SPEC(14.411).IND(3.411).NUSPEC(411).NMASS             00008190
      COMMON RMAX(3).IR(3).BK(3).NM(3).NTM(3).GPEAK(3.11)          00008200
      COMMON SPARE1.SPARE2.SPARE3.SPARE4.SPARE5.SPARE6.SPARE7      00008210
      COMMON RATMIN.RATEMX.SIGY0.SIGNXT.SIGLST                     00008220
      COMMON ISVN8.ISVN9.ISVP8.ISVP9.SIGMA7.SATVAL.SATMAX          00008230
      COMMON MODE1.MODE2.NLWCUT.NUPCUT.SATPKS(25).NSAT.EXPNAM(5)    00008240
      COMMON /CSATLS/SATLST(25).SATINX                             00008250
      COMMON /MODES/SGMODE(3).SHMODE(3).GMODE.HMODE                00008260
      COMMON /ERRORS/RMASS.ERRMAX.NERR.SIGERR.SECOND(411)          00008270
      COMMON /DUBFLG/IDUB                                          00008280
      COMMON /AJACNT/AJACEN(2)                                     00008290
      COMMON /DUBBUG/IDEBUG                                        00008300
      COMMON /CHEMPO/QDUBLT.QNORM.QSATS.NLINE                      00008310
      COMMON /QUIXOT/IQUIT                                         00008320
      COMMON /LSQ/PASS1                                            00008330
      COMMON /CRATMX/RATMXX                                        00008340
      COMMON /IMAD/MAD                                             00008350
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      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT              00008360
      EQUIVALENCE   (YVAL(1),YM5),(YVAL(2),YM4),(YVAL(3),YM3)      00008370
      EQUIVALENCE   (YVAL(4),YM2),(YVAL(5),YM1),(YVAL(6),Y0)       00008380
      EQUIVALENCE   (YVAL(7),YP1),(YVAL(8),YP2),(YVAL(9),YP3)      00008390
      EQUIVALENCE   (YVAL(10),YP4),(YVAL(11),YP5)                  00008400
      DATA HIST/-1.0,-.6667,-.3333,0.,.3333,.6667,1.,1.3333,1.6667,2./  00008410
      DATA PERCNT/.0125/                                          00008420
      DATA GTHT/'GETHGT'/                                         00008430
      DATA BEDROK/40/                                             00008440
      I1=NS-13-14*((NS-14)/14)                                    00008450
      I2=NS-12-14*((NS-13)/14)                                    00008460
      I3=NS-11-14*((NS-12)/14)                                    00008470
      I4=NS-10-14*((NS-11)/14)                                    00008480
      I5=NS-9-14*((NS-10)/14)                                     00008490
      I6=NS-8-14*((NS-9)/14)                                      00008500
      I7=NS-7-14*((NS-8)/14)                                      00008510
      I8=NS-6-14*((NS-7)/14)                                      00008520
      I9=NS-5-14*((NS-6)/14)                                      00008530
      I10=NS-4-14*((NS-5)/14)                                     00008540
      I11=NS-3-14*((NS-4)/14)                                     00008550
      I12=NS-2-14*((NS-3)/14)                                     00008560
      I13=NS-1-14*((NS-2)/14)                                     00008570
      I14=NS-14*((NS-1)/14)                                       00008580
C     *** ONLY GO HERE ON FIRST PASS TO COLLECT ANY PEAKS        00008590
C     *** THAT MIGHT HAVE BEEN INVOLVED IN A DOUBLET WITH        00008600
C     *** THE LAST COMPONENT THAT WAS PROCESSED ALSO             00008610
C     *** ZERO OUT SATURATION PARAMETERS.                        00008620
C STATEMENT BELOW HAS BEEN COMMENTED OUT BECAUSE OF CALL TO      00008630
C FUNCTION SUBROUTINE SCAN.......                                00008640
C                         RTI - WFH 11/20/78                     00008650
C     DIVIS = HIMASS - LOMASS                                    00008660
      IF ( NDIS .EQ. 2   .AND.   AJACEN(1) .EQ. 1 ) PASS1 = 0     00008670
C        MAKE SURE WE SET UP RIGHT IN BACLSQ IF WE DON'T SCAN FOR M1  00008680
      IF ( NDIS .NE. 1 ) GO TO 6                                  00008690
C     NDIS = 1 ON FIRST PASS                                     00008700
      NSAT=0                                                      00008710
      SATMAX=0                                                    00008720
      RMASS = 32000                                              00008730
      ERRMAX = 0                                                  00008740
      NERR = 0                                                    00008750
      SIGERR = 0                                                  00008760
      QNORM = 1.0                                                 00008770
      QDUBLT = 0                                                  00008780
      QSATS = 0                                                   00008790
C     HELLO JOEF DROMEY.....WHERE EVER YOU ARE...TAO             00008800
      DO 1 I = 1,411                                             00008810
1     SECOND(I) = 32767                                          00008820
      IF(OVLAP.EQ.0) GO TO 6                                     00008830
C     HERE IF OVERLAPPING ELUTANT AHEAD.                        00008840
      GMX=0.0                                                    00008850
      HMX=0.0                                                    00008860
      QDUBLT = 1                                                 00008870
C     IDUB IS FLAG FOR SETGHY                                    00008880
      IDUB = 1                                                   00008890
      DO 5 J=1,14                                                00008900
      IF(GMX.LT.GNU(J)) GMX=GNU(J)                               00008910
      IF(HMX.LT.HNU(J)) HMX=HNU(J)                               00008920
5     CONTINUE                                                   00008930
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C        NORMALIZE MODELS TO 1.0                                        00008940
         GMX=1.0/GMX                                                    00008950
         HMX=1.0/HMX                                                    00008960
         DO 7 J=1,14                                                    00008970
         GNU(J)=GNU(J)*GMX                                              00008980
         HNU(J)=HNU(J)*HMX                                              00008990
7        CONTINUE                                                       00009000
6        CONTINUE                                                       00009010
C        *** NOW START LOOPING THROUGH ALL THE SAVED MASSES            00009020
         NMS=NM(MN)                                                     00009030
         DO 500 MQ=1,411                                                00009040
         IF ( NUSPEC(MQ) .NE. -1 ) GO TO 500                            00009050
C        NUSPEC(M) NE -1 IF INTENSITIES FROM EARLIER ELUTANT HAVE       00009060
C        BEEN ALREADY COMPUTED.                                         00009070
         M=IND(MN,MQ)                                                   00009080
         IMASS = M                                                      00009090
C/       M < 0 MEANS MASS ALREADY CONSIDERED AS A COMPONENT OF PREVIOUS 00009100
C        SPECTRUM.                                                      00009110
         IF (M .LT. 0) GO TO 500                                        00009120
C        IF M = 0 THEN MASS WAS NOT DETECTED AS PEAKING IN TLOC. SO TRY 00009130
C        FOR POSSIBLE DOUBLET.                                          00009140
         IF(M.EQ.0) M = MQ                                              00009150
         MI=M+39                                                        00009160
         Y0=SPEC(I8,M)                                                  00009170
C THIS MOD MADE AT RTI BECAUSE NO POSSIBLE REASON WAS SEEN             00009180
C FOR HAVING AN EQ INSTEAD OF A GE IN                                  00009190
CTHIS SITUATION.                                                        00009200
C                          WFH - RTI 6/14/78                            00009210
         IF(Y0.GE.SATVAL) GO TO 120                                     00009220
C        IF A DUBLET IS DETECTED RUN ALL MASSES THROUGH DOUBLET RESOLVER 00009230
         IF(OVLAP.EQ.1) GO TO 130                                       00009240
C        IF IMASS IS ZERO .THEN                                         00009250
C        NO SINGLET CONTRIBUTION DETECTED IN TLOC.                      00009260
         IF(IMASS .EQ. 0) GO TO 500                                     00009270
         IF ( NDIS .EQ. 1   .AND.   AJACEN(1) .EQ. 1 ) GO TO 500        00009280
C        DON'T PROCESS ANY PASS ONE SINGLETS(MN=M1) IF A SPECTRUM       00009290
C        IMMEDIATELY PRECEDING THE CURRENTLY DETECTED SPECTRUM          00009300
C        WAS DETECTED.SINCE THIS SPECTRUM IS FOR MN=M2,                 00009310
C        AND WE DON'T WANT TO INCLUDE SINGLETS FROM PREVIOUS SPECTRUM   00009320
C        IN IT'S IMMEDIATE SUCCESSOR.                                   00009330
C             BUT, WE MUST PROCESS SATURATED PEAKS  IN ALL CASES.       00009340
         YM1=SPEC(I7,M)                                                 00009350
         YP1=SPEC(I9,M)                                                 00009360
         YM5=SPEC(I3,M)                                                 00009370
         YP5=SPEC(I13,M)                                                00009380
         YM4 = SPEC(I4,M)                                               00009390
         YP4=SPEC(I12,M)                                                00009400
         YM2=SPEC(I6,M)                                                 00009410
         YP2=SPEC(I10,M)                                                00009420
         YM3=SPEC(I5,M)                                                 00009430
         YP3=SPEC(I11,M)                                                00009440
C        PUT MASSES ON MODE OF PEAK USING CUBIC INTERPOLATION           00009450
         CALL NEWTOP(YVAL,RATEST,XTOP,YTOP,4)                           00009460
C        MAKE SURE PEAKS ARE RISING FASTER THAN BACKGROUND.             00009470
C        THIS IS A VERY MINIMAL APPROXIMATIO OF BACKGROUND.             00009480
         IF( (YTOP-YM5) .LT. 90  .AND.  (YTOP-YP5) .LT. 90 ) GOTO 500   00009490
C        *** APPLY MINIMUM RATE CRITERION FOR HIGH MASS                 00009500
C        *** PEAKS THAT CAN'T BE ISOTOPE PEAKS. TH:S ELIMINATES         00009510
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C          *** BACKGROUND PEAKS AT THE LEADING EDGE OF COMPONENTS          00009520
C          *** NOTE THE COMPUTED RATES FOR BACKGROUND PEAKS ARE            00009530
C          *** ARE ALWAYS LOW BECAUSE THEIR INTENSITY VARIATION           00009540
C          *** IS CAUSED BY A DIFFERENT PROCESS TO NORMAL MASS            00009550
C          *** CHROMATOGRAM PROFILES FOR REAL COMPONENTS.                 00009560
           IF(RATEST.LT..095) GO TO 500                                   00009570
           IF(M .LT. 140) GO TO 25                                        00009580
           IF(RATEST .LT. RATMIN)  GO TO 500                              00009593
C          *** CORRECT FOR FINITE SWEEP OFFSET                            00009600
C          *** REJECT ODDBALL PEAK-MODES                                  00009610
25         CONTINUE                                                       00009620
30         CONTINUE         .                                            00009630
C          *** HERE FOR EXCLUSION TEST ON PEAK TOP RELATIVE TO            00009640
C          *** HISTOGRAM MODE - IF "IH" IS OUTSIDE LIMITS THEN            00009650
C          *** PEAK IS REJECTED.                                          00009660
           IF(XTOP .LE. -1.5  .OR.  XTOP .GE.  1.5) GO TO 500             00009670
C          THE ABOVE REJECTS ANY PEAKS WITH FUNNY SHAPES, OR MODES NOT    00009680
C          IN HISTOGRAMMIC WINDOW.                                        00009690
           MI=M+39                                                        00009700
           MI=M+39                                                        00009700
C FUNCTION SUBROUTINE CALL HAS BEEN SUBSTITUTED FOR ARITHMETIC            00009710
C IN ORDER TO ACCOMODATE MAGNETIC INSTRUMENTS...                          00009720
C                                     RTI - WFH 11/20/78                  00009730
C          TSHIFT = (MI - LOMASS)/DIVIS                                   00009740
           TSHIFT = SCAN(MI)                                              00009750
          .XTOP = XTOP + TSHIFT                                           00009760
           DO 600 IJ = 1,10                                               00009770
           IF(XTOP .LT. HIST(IJ)) GO TO 700                               00009780
600        CONTINUE                                                       00009790
700        IH = IJ + (NDIS-1) * 3  -  4                                   00009800
C          IH IS IN ONE THE THREE SETS ↑-3 TO 60, ↑0 TO 90, ↑3 TO 120     00009810
C               AS A FUNTION OF NDIS = 1,2,3                              00009820
C          SEE IF HISTOGRAM INDEX IS OUT OF RANGE OF DETECTED SPECTRUM    00009830
C          **** BELOW USED TO SAY IH.GE.NLWCUT****12/19 CHANGED           00009840
           IF(IH.LT.NLWCUT.OR.IH.GT.NUPCUT) GO TO 500                     00009850
C          WE NOW SEE IF THE DATA WILL PASS OVER A FLOOR                  00009860
C          BELOW YTOP.                                                    00009870
           FLUSH = PERCNT * YTOP                                          00009880
           BUBBLE = PERCNT * G(5)                                         00009890
C        ' GET  MAX↑ FLUSH,BUBBLE @                                       00009900
           IF ( FLUSH .LT. BUBBLE ) FLUSH = BUBBLE                        00009910
C          GET MIN↑ 70,FLUSH @                                            00009920
           IF ( 70 .LT. FLUSH ) FLUSH = 70                               00009930
C          GET MAX ↑ BEDROK,FLUSH @                                       00009940
           IF ( BEDROK .GT. FLUSH ) FLUSH = BEDROK                        00009950
           FLOOR = YTOP - FLUSH                                           00009960
C                        *                                               00009970
C                                                                        00009980
C                                                                        00009990
C                                                                        00010000
C                                                               00010010
C          YM3         YTOP          YP3                                 00010020
C   ...................................................... ← FLOOR       00010030
C    IF THE CURVE STAYS ABOVE THE FLOOR IT GETS FLUSHED                  00010040
           DO 110 II = 3,9                                               00010050
           IF ( YVAL(II) .LE. FLOOR )   GO TO 111                        00010060
110        CONTINUE                                                      00010070
           GO TO 500                                                     00010080
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C        ....      AND AWAY WE GOOOOOOOOOOOOOOOO ..... BLUB ...       00010090
111      CONTINUE                                                     00010100
         CALL BLEED(YVAL(3),OITAR)                                    00010110
C                                                                     00010120
C THIS IS A TEMPORARY MOD IN ORDER TO GATHER STATICS ON              00010130
C THE INPUT PARAMETER ERRATIO - CODE 2                               00010140
C                              WFH RTI 9/31/78                        00010150
C        ISPC=SPCNO                                                   00010160
C        ITYP=2                                                       00010170
C        WRITE(20,6250) ITYP,ISPC,OITAR,OITAR                        00010180
C6250 FORMAT(A4,A4,16X,A4,4X,A4)                                     00010190
         IF ( OITAR .LT. RATMXX ) GO TO 500                          00010200
C        THE ABOVE FITS A LINE TO YM3 THRU YP3, AND                  00010210
C        RETURNS OITAR = (MEAN SQUARE ERR)/(AVERAGE VALUE Y )        00010220
C        *** THROW AWAY MASS INDEX SO THAT IT CAN'T BE INCLUDED      00010230
C        *** IN SPECTRUM OF NEXT-DETECTED COMPONENT                  00010240
         IND(MN,MO)= -1                                              00010250
C        PUT MASSES ON SAME TIME CO-ORDINATE AS MODEL                00010260
         CALL TIMESF(TSHIFT,YVAL,11,GMODE)                           00010270
C        *** NOW COMPUTE AND REMOVE LINEAR BACKGROUND BY             00010280
C        *** LEAST SQUARES METHOD USING MODEL PEAK - THE             00010290
C        *** CORRECTED INTENSITY IS RETURNED AS "PKHGT"              00010300
         CALL BACLSQ(PKHGT)                                          00010310
C         PEAKS OF INTENSITY < 10 ARE CONSIDERED AS ARTIFACTS OF     00010320
C        THE SINGLET RESOLVER                                        00010330
         IF( PKHGT .LT. 10 ) GO TO 500                               00010340
         NUSPEC(M)=PKHGT                                             00010350
         GO TO 500                                                   00010360
C        *** HERE FOR HANDLING SATURATED PEAKS BY RATIO             00010370
C        *** APPROACH THAT USES NON - SATURATED VALUES OF PEAK      00010380
C        *** TOGETHER WITH THE MODEL PEAK FOR THE COMPONENT TO      00010390
C        *** COMPUTE THE AMPLITUDE (LESS BACKGROUND) OF THE         00010400
C        *** SATURATED PEAK. JUMP OVER IF SATURATED PEAK HAS BEEN   00010410
C        *** PROCESSED IN AN EARLIER PASS BY "GETHGT"               00010420
120      CONTINUE                                                    00010430
         NUSE  = NUSPEC(M)                                           00010440
         IF( NUSE .LT. 0  .AND.  NUSE .NE. -1 ) GO TO 500            00010450
C        NUSE < 0 IF THIS PEAK HAS BEEN PROCESSED IN EARLIER PASS    00010460
C        NOTE: IF NUSE = -1 IT HASN'T BEEN PROCESSED YET.           00010470
         IF(NSAT.GE.25) GO TO 500                                    00010480
         NSS=NS+2-NDIS                                               00010490
         CALL SATLSQ(NSS,M,RPKHGT,G,SPEC,SATVAL,MODEL,OVLAP,MODE2,PKHIST) 00010500
C        *** SAVE COMPUTED HEIGHT FOR LATER SO THAT IT CAN BE       00010510
C        *** NORMALIZED TO INTEGER SIZE                             00010520
         IF ( IQUIT .EQ. 1 ) GO TO 500                               00010530
C        IQUIT = 1 IF SATURATED VALUES MODE IS NOT "NEAR"           00010540
C        SPECTRUM.                                                  00010550
C        IQUIT = 2 IF WE WANT TO SKIP PEAK BECAUSE IT DOESN'T       00010560
C        BELONG IN THIS SPECTRUM. IT WAS IN OVERLAPPING PREDECESSOR. 00010570
         IF ( IQUIT .NE. 2 ) GO TO 125                               00010580
         NUSPEC(M) = -2                                              00010590
         GO TO 500                                                   00010600
125      CONTINUE          .                                         00010610
         NSAT=NSAT+1                                                 00010620
         SATPKS(NSAT)=RPKHGT                                         00010630
C        RPKHGT IS < 0 IF SUPERSATURATION ENCOUNTERED               00010640
         NUSPEC(M)= -NSAT - 2                                        00010650
C        SAVE MAXIMUM SATURATED VALUE ENCOUNTERED FOR NORMALIZATION  00010660
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          IF(SATMAX.GT.RPKHGT) GO TO 500                              00010670
          SATMAX=RPKHGT                                               00010680
          GO TO 500                                                   00010690
C         *** HERE FOR HANDLING DOUBLETS IN THE SET                   00010700
130       CONTINUE                                                    00010710
C         RUN ALL MASSES THROUGH DOUBLET RESOLVER IF OVLAP=1,IE,      00010720
C         DOUBLET SITUATION DETECTED.                                 00010730
          IGPOS=MODE1                                                 00010740
          IHPOS=MODE2                                                 00010750
C         NSD=NS+3-NDIS                                               00010760
          IF(NDIS .NE. 2) GO TO 500                                   00010770
C         ONLY GO THROUGH DOUBLET RESOLVER WHEN WE ARE LOOKING AT     00010780
C         "SPECTRUM 7".                                               00010790
          CALL SETGHY(NS,M,GNU,HNU,IGPOS,IHPOS,IDUB,GMX)              00010800
C         DO NOT MARK MASS AS ALREADY FOUND "CONTRIBUTION" BY SETTING 00010810
C           IND(MN,MO) = 0,                                           00010820
C         SINCE THE DUBLET RESOLVER SAVES THE LARGEST CONTRIBUTION IN 00010830
C         THE ARRAY NUSPEC(M).                                        00010840
500       CONTINUE                                                    00010850
C         *** HERE ONLY ON THIRD PASS AND ONLY THEN IF ANY            00010860
C         *** SATURATED PEAKS HAVE BEEN FOUND. NEED TO NORMALIZE      00010870
C         *** SO THAT EXTRAPOLATED VALUES CAN BE SAVED AS INTEGERS    00010880
          IF( NSAT .EQ. 0    .OR.   NDIS .NE. 3 ) RETURN              00010890
C         SET LOWER BOUND ON SATINX.THIS ARRAY IS USED IN SATLSQ.     00010900
          J = 26                                                      00010910
          DO 723 I = 1,25                                             00010920
          J = J - 1                                                   00010930
          IF ( SATLST(J) .NE. 0 ) GO TO 750                           00010940
723       CONTINUE                                                    00010950
750       CONTINUE                                                    00010960
          SATINX = J                                                  00010970
          AMXNU=0.0                                                   00010980
C         GET MAXIMUM VALUE IN SPECTRUM                               00010990
          DO 503 J=1,411                                              00011000
          IF(NUSPEC(J).GT.AMXNU) AMXNU=NUSPEC(J)                      00011010
503       CONTINUE                                                    00011020
C         SATMAX WILL BE 0 IF ONLY SUPERSATURATION ENCOUNTERED..      00011030
          IF ( SATMAX .EQ. 0 ) SATMAX = SATVAL                        00011040
          IF(AMXNU.GT.SATMAX) SATMAX=AMXNU                            00011050
          AMXNU = SATMAX                                              00011060
C         NORMALIZE TO 32000                                          00011070
          SATMAX=32000.0/SATMAX                                       00011080
C         NUSPEC(J) < 0 IF SATURATED VALUE FOR THAT MASS              00011090
          DO 530 J=1,411                                              00011100
          IF(NUSPEC(J)) 510,530,520                                   00011110
C         HERE IF SATURATED VALUE                                     00011120
510       IF ( NUSPEC(J) .EQ. -1 ) GO TO  530                         00011130
          IF ( NUSPEC(J) .EQ. -2 ) GO TO  530                         00011140
          NC = -NUSPEC(J) - 2                                         00011150
C         SATPKS(NC) < 0    IF SUPER SATURATION.                      00011160
          IF ( SATPKS(NC) .LT. 0 ) SATPKS(NC) = AMXNU                 00011170
          NUSPEC(J)=SATPKS(NC)*SATMAX                                 00011180
          QSATS = QSATS + 1                                           00011190
C         *** USE C13 ISOTOPE TO ASSIGN SATURATED PEAK TO THE         00011200
C         *** APPROPRIATE COMPONENT WHEN THERE ARE TWO COMPONENTS  .  00011210
C         *** CLOSE TOGETHER                                          00011220
C         OVLAP = 0 MEANS NO ELUTANT DETECTED AHEAD AND CLOSE         00011230
          IF( OVLAP .EQ. 0 )  GO TO 530                               00011240
```

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C        NUSPEC(J+1) NOT EQUAL ZERO MEAN ISOTOPE PRESENT IN THIS      00011250
C        ELUTANT                                                      00011260
         IF ( NUSPEC(J+1) .EQ. 0 ) GO TO 511                          00011270
         IF ( NUSPEC(J+1) .EQ. -1 ) GO TO 511                         00011280
         GO TO 530                                                    00011290
511      NUSPEC(J) = 0                                                00011300
         MY = J + 39-MAD                                              00011310
         QSATS = QSATS - 1                                            00011320
         IF ( IDEBUG .EQ. 0 ) GO TO 530                               00011330
         WRITE(IPTR2,1000) MY                                         00011340
         GO TO 530                                                    00011350
520      NUSPEC(J)=NUSPEC(J)*SATMAX                                   00011360
530      CONTINUE                                                     00011370
         IF ( QSATS .GE. 1 ) QNORM = SATMAX                           00011380
         RETURN                                                       00011390
C3222    FORMAT(//' AJACENT FLAG =',I3//)                             00011400
1000     FORMAT(/,' MASS ',I3,' HAS NO C13 ISOTOPE PEAK ',//)         00011410
         END                                                         00011420
         SUBROUTINE KAPUT( SPECNO,TOTION,TICRAT,ABMAX )               00011430
         REAL TOTION,ABMAX                                            00011440
         INTEGER SPECNO,TICRAT                                        00011450
         COMMON /SLOTNO/NSLOT                                         00011460
         COMMON /CFSTPG/FSTPGE                                        00011470
         COMMON /CHEMPO/QDUBLT,QNORM,QSATS,NLINE                      00011480
         COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT               00011490
         INTEGER  QDUBLT,QSATS,NLINE,ITOTS,NSLOT,FSTPGE               00011500
         REAL     QNORM                                               00011510
         REAL     YES1/' ',YES/'YES ',YNOY/' NO '/                    00011520
C        THIS ROUTINE DOES THE CHEMIST'S PRINTOUT                     00011530
C        QDUBLT            1 IF THE SPECTRA IS FIRST ELUTANT OF DUBLET.00011540
C        QSATS             NO. OF SATURATED PEAKS IN SPECTRUM.        00011550
C        NLINE             LINE COUNT FOR EACH PAGE.                  00011560
C        SPECNO            SPECTRUM NUMBER                            00011570
C        TOTION            TOTAL ION CURRENT OF SPECTRUM.             00011580
C        TICRAT            CLEANUP RATIO(SEE OUTDAT FOR DETAILS).     00011590
C        ABMAX             MAXIMUM AMPLITUDE OF SPECTRUM.             00011600
         NSLOT = NSLOT + 1                                            00011610
         IF(NSLOT.EQ.1)WRITE(IPTR3,1000)                             00011620
         YES1=YES                                                     00011630
         IF ( QDUBLT .EQ. 0 )YES1=YNOY                                00011640
         WRITE(IPTR3,2000) NSLOT,SPECNO,TOTION,TICRAT,ABMAX,YES1,QSATS 00011650
         RETURN                                                       00011660
1000     FORMAT(' SLOT  SPEC.#       TOTION  TICRAT  MAX. AMP  DOUBLET?00011670
        *SAT. PEAKS '//)                                              00011680
2000     FORMAT(3X,I3,5X,I5,3X,F8.0,3X,I3,4X,F8.0,4X,A4,6X,I3)        00011690
         END                                                         00011700
         SUBROUTINE LKAHED(NS,M2,M3,OVLAP,G,H)                        00011710
C                                                                     00011720
C        THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT 00011730
C        FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND    00011740
C        GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00011750
C        (GRANT NGR-05-020-632).                                      00011760
C                                                                     00011770
C                                                                     00011780
C        *** THIS ROUTINE USES THE SAME TECHNIQUES AS 'TLOC'          00011790
C        *** TO LOOK BEYOND THE PROCESSING WINDOW AND DETECT          00011800
C        *** IF THERE ARE ANY NEW COMPONENTS NEARBY. THIS IS          00011810
C        *** IMPORTHNT FOR COMPENSATING FOR OVERLAP                   00011820
```

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C      *** INTERRACTIONS USING THE DOUBLET RESOLVER.           00011830
C      *** A MODEL PEAK IS SELECTED FOR ANY COMPONENT THAT      00011840
C      *** IS COMING UP DIRECTLY. THE RELATIVE DISTANCE         00011850
C      *** BETWEEN NEIGHBORING COMPONENTS IS ESTABLISHED        00011860
C      *** ACCURATELY FROM THE LOCAL HISTOGRAM PROFILES.        00011870
C                                                               00011880
       REAL     ISVP8,ISVP9                                     00011890
       INTEGER NAME,RDATE,BITMAP,GCTIME,LIBMAP,INTEG,LOMASS     00011900
       INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO   00011910
       INTEGER SPEC,IND,IR,BK,NM,NTM,BUBBLE                     00011920
       INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7         00011930
       REAL    SPARE5,SPARE6                                    00011940
       INTEGER NUSPEC,NMASS,OVLAP                               00011950
       INTEGER NSP2,NSP3,NT2,NT3,SCNDPK,NERR,SECOND             00011960
       REAL NXTRTE,RASS,ERRMAX,SIGERR                           00011970
C                                                               00011980
       DIMENSION SCNDPK(3,11),NXTRTE(3),H(11),G(9)              00011990
       COMMON PKHIST(20),NPHIST(20)                             00012000
       COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5        00012010
       COMMON GM4(9)                                            00012020
       COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                  00012030
       COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME               00012040
       COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT      00012050
       COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                      00012060
       COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS         00012070
       COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)      00012080
       COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7  00012090
       COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                 00012100
       COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX      00012110
       COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5) 00012120
       COMMON /CAHEA/AHEAD(5)                                   00012130
       COMMON /ERRORS/RASS,ERRMAX,NERR,SIGERR,SECOND(411)       00012140
       COMMON /MODES/ SGMODE(3),SHMODE(3),GMODE,HMODE           00012150
       COMMON /IFF/JFLAG(3)                                     00012160
       COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                  00012170
       COMMON /MASSES/ISGMAS(3),ISHMAS(3),IGMASS,IHMASS         00012180
       COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT           00012190
       INTEGER ONE,TWO,THREE,FOUR,FIVE,SIX,UNION,AHEAD          00012200
       DIMENSION IFLAG(3)                                       00012210
C                                                               00012220
C                                                               00012230
       REAL*8 ILKA                                              00012240
       DATA ONE/ 1/,TWO/2/,THREE/3/,FOUR/4/,FIVE/5/,SIX/6/      00012250
       DATA ILKA/'LKAHED'/                                      00012260
C      ***************************************************      00012270
       DO 3 I=12,20                                             00012280
       NPHIST(I)=0                                              00012290
       PKHIST(I)=0                                              00012300
3      CONTINUE                                                 00012310
       DO 4 I=1,25                                              00012320
4      SATPKS(I)=0.0                                            00012330
       NSHIFT=0                                                 00012340
       NSP2=NS+1                                                00012350
C       REINITIALIZE ARRAY FOR SAVING SPECTRUM                  00012360
       DO 5 M=1,411                                             00012370
5      NUSPEC(M)= -1                                            00012380
       UNION = 0                                                00012390
       IF(OVLAP.EQ.0) GO TO 7                                   00012400
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C       OVLAP SET MEANS PRECEDING SPECTRUM CONTRIBUTED TO THIS ONE.    00012410
        OVLAP=0                                                        00012420
        UNION = 1                                                      00012430
C       UNION IS SET TO INDICATE WE WILL UNION SPECTRUM N-1'S          00012440
C       CONTRIBUTIONS WITH SPECTRUM N ONLY IF SPECTRUM N               00012450
C       DOESN'T HAVE AN OVERLAPPING ELUTANT.                           00012460
7       CONTINUE                                                       00012470
        CALL NXTMAX(SPEC,NSP2,RNS2,YNS2,NT2,SATVAL                     00012480
     &     ,SCNDPK,NXTRTE,NSHIFT,IFLAG)                                00012490
        NSHIFT=1                                                       00012500
        NSP3=NS+2                                                      00012510
        CALL NXTMAX(SPEC,NSP3,RNS3,YNS3,NT3,SATVAL                     00012520
     &     ,SCNDPK,NXTRTE,NSHIFT,IFLAG)                                00012530
        NSHIFT=2                                                       00012540
        NSP4=NS+3                                                      00012550
        CALL NXTMAX(SPEC,NSP4,RNS4,YNS3,NT4,SATVAL                     00012560
     &     ,SCNDPK,NXTRTE,NSHIFT,IFLAG)                                00012570
C       SCAN FROM   MODE1 + NTHIRD   TO 13. SINCE THE CURRENT SPECTRUM 00012580
C       EFFECTS HIST(2-8)  WITH MODE1 VARYING FROM 4 TO 6.             00012590
C       LOOKING FOR SPECTRUM IN *MODE1+NTHIRD,9 @                      00012600
        NL=MODE1 + NTHIRD                                              00012610
C       SEE IF WE HAVE TO SCAN TOO CLOSE ( *7,8,9@)                    00012620
        IF ( NL .GE. 10 ) GO TO 10                                     00012630
C       SO NL .LE. 9                                                   00012640
        IDXL = NL                                                      00012650
        IDXU = 9                                                       00012660
        NU = 10                                                        00012670
        IAHEAD = 2                                                     00012680
        CALL DETEKT(PKHIST,NPHIST,OVLAP,NLWCUT,NUPCUT,NL,NU,IDXL  ,IDXU,MO00012690
     *DE2)                                                             00012700
        IF ( OVLAP .EQ. 1 ) GO TO 26                                   00012710
C       SCAN *9,13@ FOR ELUTANT IN *10,12@                            00012720
        NL = 9                                                         00012730
10      IF ( NL .GE. 13 ) GO TO 20                                     00012740
        IAHEAD = 3                                                     00012750
        NU=13                                                          00012760
        IDXL=10                                                        00012770
        IDXU=12                                                        00012780
        CALL DETEKT(PKHIST,NPHIST,OVLAP,NLWCUT,NUPCUT,NL,NU,IDXL       00012790
     &     ,IDXU,MODE2)                                                00012800
        IF(OVLAP.EQ.1) GO TO 26                                        00012810
C       SEE IF SPECTRUM AHEAD IN *13,15@                              00012820
20      NL = 12                                                        00012830
        NU =16                                                         00012840
        IDXL = 13                                                      00012850
        IDXU = 15                                                      00012860
        IAHEAD = 4                                                     00012870
        CALL DETEKT(PKHIST,NPHIST,OVLAP,NLWCUT,NUPCUT,NL,NU,IDXL,IDXU,MODE00012880
     *2)                                                               00012890
        IF ( OVLAP .EQ. 1 ) GO TO 26                                   00012900
C       SEE IF SPECTRUM AHEAD IN *16,18@                              00012910
        NL = 15                                                        00012920
        NU = 19                                                        00012930
        IDXL = 16                                                      00012940
C       IDXL =18                                                       00012950
C THIS SEEMED AN OBVIOUS TYPO, SO IDXL HAS BEEN CHANGED               00012960
C TO IDXU AS IN THE STMT BELOW                                        00012970
C                              WFH RTI 9/31/78                        00012980
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          IDXU = 18                                                      00012990
          IAHEAD = 5                                                     00013000
          CALL DETEKT(PKHIST,NPHIST,OVLAP,NLWCUT,NUPCUT,NL,NU,IDXL,IDXU,MODE00013010
         *2)                                                             00013020
          IF ( OVLAP .EQ. 0 ) GO TO 30                                   00013030
26        CONTINUE                                                       00013040
          AHEAD(IAHEAD) = 1                                              00013050
C     SET SPECTRUM AHEAD FLAG                                            00013060
30        CONTINUE                                                       00013070
          RC0 = .5                                                       00013080
          RATEMX = RMAX(M2)                                              00013090
          RATMIN = RATEMX * 0.25  * RC0                                  00013100
          GMODE =SGMODE(M2)                                              00013110
          JFLAG1 = JFLAG(M2)                                             00013120
          IGMASS = ISGMAS(M2)                                            00013130
C     STORE MODEL PEAK FOR THIS SPECTRUM                                 00013140
          DO 2000 IJ=1,9                                                 00013150
2000      GM4(IJ) = GPEAK(M2,IJ+1)                                       00013160
          IF(OVLAP.EQ.0) GO TO 95                                        00013170
C     HERE FOR OVERLAPPING SPECTRUM DOWN THE PIPE                        00013180
          MODEH=6+(MODE2-1)/3                                            00013190
C       MODEH IS RELATIVE SPECTRUM NUMBER OF OVER LAPPER.                00013200
C LABEL 40 HAS BEEN PUT TO BETTER USE....                               00013210
C                              RTI WFH 11/20/78                          00013220
          IF(MODEH-10) 50,60,70                                          00013230
50        INDXH=1                                                        00013240
          GO TO 80                                                       00013250
60        INDXH=2                                                        00013260
          GO TO 80                                                       00013270
70        INDXH=3                                                        00013280
80        CONTINUE                                                       00013290
          SH=0.0                                                         00013300
C     STORE MODEL H                                                      00013310
C THIS MOD INSERTED TO HELP WITH POOR INITIALIZATION                     00013320
C OF H-PEAK PARAMETERS.......                                            00013330
C                              RTI WFH 11/20/78                          00013340
          IF(ISHMAS(INDXH).NE.-1)GO TO 40                                00013350
          OVLAP = 0                                                      00013360
          RETURN                                                         00013370
    40 IF ( MODEH .NE. 8 ) GO TO 89                                      00013380
C     IF SPECTRUM ELUTING AT SLOT 8,GIVE IT DETECTED THERE.              00013390
          DO 88 I = 1,11                                                 00013400
          H(I) = GPEAK(M3,I)                                            00013410
88        SH = SH + H(I)                                                 00013420
          IHMASS = ISGMAS(M3)                                            00013430
          HMODE = SGMODE(M3)                                             00013440
          IFLAG(INDXH) = JFLAG(M3)                                       00013450
          GO TO 91                                                       00013460
89        CONTINUE                                                       00013470
          HMODE = SHMODE(INDXH)                                          00013480
          IHMASS = ISHMAS(INDXH)                                         00013490
          DO 90 I=1,11                                                   00013500
          H(I) = SCNDPK(INDXH,I)                                         00013510
          SH=SH + H(I)                                                   00013520
90        CONTINUE                                                       00013530
91        CONTINUE                                                       00013540
C     SEE IF WEIRD H MODEL PEAK.                                         00013550
          IF ( SH .LE. 0 ) OVLAP = 0                                     00013560
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      IF ( SH .LE. 0 ) GO TO 95                                       00013570
      CALL TIMESF( HMODE,H,11,GMODE )                                 00013580
C     ALIGN H-MODEL TO G-MODEL'S TIME CO-ORDINATE.                    00013590
C        .. ANOTHER VOID .. EH       DOGEN ..                         00013600
95    CONTINUE                                                        00013610
C     SEE IF PREVIOUS SPECTRUM OVERLAPPED WITH THIS ONE.              00013620
      IF ( UNION .EQ. 0 ) GO TO 27                                    00013630
      BUBBLE = .01 * GM4(5)                                           00013640
C     UNION = 0 IF PREVIOUS ELUTANT NOT OVERLAPPING WITH THIS ONE.    00013650
C     WE WANT TO MAKE SURE THOSE "SMALL CONTRIBUTIONS"                00013660
C     WHEN CALCULATING THE CURRENT  SPECTRUM USING                    00013670
C     THE DUBLET RESOLVER IN CONJUNTION WITH THE PREVIOUS             00013680
C      OVERLAPPING ELUTANT GET USED IF WE ARE AGAIN IN                00013690
C     AN OVERLAPPING SITUATION.                                       00013700
      IF ( OVLAP .EQ. 0 ) GO TO 29                                    00013710
C     ONLY DO BELOW IF DOUBLET IS AGAIN A DOUBLET                     00013720
      DO 28 M = 1,NMASS                                               00013730
28    IF ( SECOND(M) .LE. BUBBLE ) NUSPEC(M) = 0                      00013740
      GO TO 27                                                        00013750
C     OVLAP = 1, SO AGAIN IN OVERLAPPING SITUATION. DON'T UNION       00013760
C     N-1 WITH N. RATHER, CALCULATE N'S SPECTRUM(EXCEPT FOR           00013770
C     ZERO CONTRIBUTIONS FROM N-1) USING DUBLET RESOLVER.             00013780
29    CONTINUE                                                        00013790
C     OVERLAP = 0 SO NO DUBLET SITUATION.THEREFORE UNION.             00013800
C     SINCE UNION = 1 WE'LL  UNION SPECTRUM N-1'S CONTRIBUTIONS       00013810
C     WITH OUR CURRENT SPECTRUM. N.                                   00013820
      DO 6 M = 1,411                                                  00013830
      IF ( SECOND(M) .LE. 10 )    SECOND(M) = 0                       00013840
6     IF ( SECOND(M) .NE. 32767 ) NUSPEC(M) = SECOND(M)               00013850
27    CONTINUE                                                        00013860
      DO 2400 IJ=1,9                                                  00013870
2400  G(IJ)=GM4(IJ)                                                   00013880
      CALL LKAPRT(7,NPHIST,PKHIST)                                    00013890
C     THE ABOVE PRINTS THE SECOND HALF OF THE HISTOGRAMS.             00013900
      IF(JFLAG1 .EQ. 1) CALL LKAPRT(FIVE,I,R)                         00013910
C     THIS HAPPENS IF THE MODEL IS FLAGGED AS FUNNY IN TLOC           00013920
      CALL LKAPRT(THREE,IGMASS,G)                                     00013930
C     PRINT MODELS                                                    00013940
      IF(OVLAP .EQ. 0) RETURN                                         00013950
      CALL LKAPRT(ONE,I,R)                                            00013960
C     THE ABOVE  PRINTS 'OVERLAPPING SPECTRUM FOUND' MSG.             00013970
      IF(MODEH.GE.9.AND.MODEH.LE.11) GOTO 401                         00013980
C     THE BELOW WRITES MODEH AS A WARNING THAT THE SECOND             00013990
C        ELUTANT IS VERY CLOSE                                        00014000
      CALL LKAPRT(TWO,MODEH,H)                                        00014010
401   CONTINUE                                                        00014020
C     MODEH = 12 ONLY IF NEXT MAX IS IN SLOTS 19,20 OF HISTOS.        00014030
      CALL LKAPRT( FOUR,IHMASS,H(2) )                                 00014040
C     SEE IF FLAKEY MODEL WAS USED FOR INTERPOLATION                  00014050
      IF(IFLAG(INDXH) .EQ. 1) CALL LKAPRT(SIX,I,H)                    00014060
      RETURN                                                          00014070
      END              .                                              00014080
C     THE CALL STATEMENT ALLOWS FOR PASSING OF ARRAYS                 00014090
C     REALS AND INTEGERS.                                             00014100
C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT    00014110
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND       00014120
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00014130
C     (GRANT NGR-05-020-632).                                         00014140
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      SUBROUTINE LKAPRT(N,IAR,AR)                                    00014150
      INTEGER N,IONE,NINE,MAD,IIAR(20)                               00014160
      INTEGER IAR(1)                                                 00014170
      REAL AR(1)                                                     00014180
      COMMON /DUBBUG/IFLAG                                           00014190
      COMMON /IMAD/MAD                                               00014200
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                 00014210
      DATA IONE,NINE/1,9/                                            00014220
C        IFLAG IS RESET IF NO PRINTING IS TO BE DONE/               00014230
      IF (IFLAG.EQ.0) RETURN                                        00014240
      IIAR(1)=IAR(1)-MAD                                            00014250
      IF(IIAR(1).LT.0)IIAR(1)=0                                     00014260
      GO TO (80,90,100,110,120,130,140),N                          00014270
C        THE ABOVE IS A CASE STATEMENT FOR EXECUTING PRINT          00014280
80    WRITE(IPTR2,580)                                             00014290
      RETURN                                                        00014300
C     THE ABOVE  WRITE IS CALLED FROM LKAHED(BELOW ALSO)            00014310
90    WRITE(IPTR2,590) IIAR(1)                                      00014320
      RETURN                                                        00014330
100   WRITE(IPTR2,1000) (AR(I), I = IONE,NINE),IIAR(1)             00014340
      RETURN                                                        00014350
110   WRITE(IPTR2,1100) (AR(I), I = IONE,NINE),IIAR(1)             00014360
      RETURN                                                        00014370
120   WRITE(IPTR2,1200)                                            00014380
      RETURN                                                        00014390
130   WRITE(IPTR2,1300)                                            00014400
      RETURN                                                        00014410
140   WRITE(IPTR2,1500)                                            00014420
      DO 5 K=2,18                                                   00014430
      IIAR(K)=IAR(K)-MAD                                            00014440
      IF(IIAR(K).LT.0)IIAR(K)=0                                     00014450
5     CONTINUE                                                      00014460
      WRITE(IPTR2,530) (IIAR(I), I = 10,18 )                       00014470
      WRITE(IPTR2,535) ( AR(I), I = 10,18 )                        00014480
C       WRITES SECOND HALF OF HISTOGRAMS.                           00014490
      RETURN                                                        00014500
500   FORMAT(/,' OVERLAPPING SPECTRUM FOUND')                      00014510
590   FORMAT(' OVERLAPPING ELUTANT IS CLOSE, RELATIVE SPEC. =',I4) 00014520
1000  FORMAT(/,' MODEL USED FOR SINGLET RESOLUTION ',/,9F9.0,      00014530
     -//,' MASS OF MODEL =',I3)                                     00014540
1100  FORMAT(/' MODEL USED FOR DOUBLET RESOLUTION ',/,9F9.0,       00014550
     -//' MASS OF MODEL = ',I3,/,'   NOTE: THIS MODEL HAS BEEN'    00014560
     -,' INTERPOLATED TO THE MASS OF THE SINGLET MODEL')           00014570
1200  FORMAT(' *** WARNING *** THIS SPECTRUM HAS A SUSPECT G-MODEL '00014580
     -,'PEAK'/,'   POSSIBLE BACKGROUND PEAK USED AS MODEL'/        00014590
     -,'    EXAMINE MODEL USING  LOOK  IF YOU ARE WARY'/)          00014600
1300  FORMAT(' *** WARNING *** THIS SPECTRUM HAS A SUSPECT H-MODEL '00014610
     -,'PEAK'/,'   POSSIBLE BACKGROUND PEAK USED AS MODEL'/        00014620
     -,'    EXAMINE MODEL USING  LOOK  IF YOU ARE WARY'/)          00014630
535   FORMAT(1X,9F9.0)                                             00014640
530   FORMAT(/,' PEAK HIST ',/,8X,9I6//' ION CURRENT HIST ')       00014650
1500  FORMAT(//' HISTOGRAM POSITIONS 10 - 18 ...'/)                00014660
      END                                                           00014670
      SUBROUTINE NEWTOP(Y,RATE,XTOP,YTOP,ISTART)                   00014680
      REAL    RATE,XTOP                                            00014690
      DIMENSION    Y(11)                                           00014700
      INTEGER   ISTART                                             00014710
C                                                                  00014720
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C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT        00014730
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND           00014740
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION     00014750
C     (GRANT NGR-05-020-632).                                            00014760
C                                                                        00014770
C     THIS SUBROUTINE INTERPOLATES A PEAK TO THE MODE OF A PARABOLA       00014780
C     THRU THE MIDDLE 5 POINTS. THE MODE IS FOUND USING A PARABOLIC       00014790
C     LEAST SQUARE FIT THROUGH THE MIDDLE FIVE Y'S , THEN                 00014800
C     SOLVING FOR THE X DISPLACEMENT OF THE MODE  FROM 0.                 00014810
C                                                                        00014820
C         SO, IF Y = A + B * X + C * X**2                                00014830
C                                                                        00014840
C     X = -B/2C IS THE DISPLACEMENT.                                     00014850
C                       Y                                                00014860
C                       *                                                00014870
C                       :            *                                   00014880
C               *       :  :                                             00014890
C                       :                                                00014900
C                       :              *                                 00014910
C        *         :                                                     00014920
C     ................:.....................  X                          00014930
C                 0    -B/2C                                             00014940
C                                                                        00014950
C     THE INTERPOLATION IS DONE BY A CUBIC FIT USING  LAGRANGE'S         00014960
C     METHOD.I.E., GIVEN THE 4 POINTS  X0,X1,X2,X3, WE FIND L(X) AS      00014970
C     FOLLOWS:                                                           00014980
C                                                                        00014990
C         L(X)=+(X-X1)(X-X2)(X-X3)/((X0-X1)(X0-X2)(X0-X3))@Y0 +          00015000
C              +(X-X0)(X-X2)(X-X3)/((X1-X0)(X1-X2)(X1-X3))@Y1 +          00015010
C              +(X-X0)(X-X1)(X-X3)/((X2-X0)(X2-X1)(X2-X3))@Y2 +          00015020
C              +(X-X0)(X-X1)(X-X2)/((X3-X0)(X3-X1)(X3-X2))@Y3            00015030
C                                                                        00015040
C         WITH THE X'S INTEGRALLY SPACED.                               00015050
C                                                                        00015060
C     IN EACH CASE WE INTERPOLATE FOR A NEW MIDDLE POINT,OR             00015070
C     L(X1+DX). SO, THE ABOVE EQUATION REDUCES TO                        00015080
C                                                                        00015090
C         L(X1+DX) = C0 * Y0 + C1 * Y1 + C2 * Y2 + C3 * Y3              00015100
C                                                                        00015110
C     C0 = DX * (DX-1)(DX-2)/-6                                         00015120
C     C1 = (DX+1)(DX-1)(DX-2)/2                                         00015130
C     C2 = (DX+1)(DX)(DX-2)/-2                                          00015140
C     C3 = (DX+1)(DX)(DX-1)/6                                           00015150
C                                                                        00015160
C     WHERE DX = -B/2C                                                  00015170
C                                                                        00015180
C THIS ROUTINE HAS BEEN CHANGED SO THAT Y(I) ARE UNCHANGED              00015190
C AND A SMOOTHED RATE IS CALCULATED FROM THE WORK ARRAY Z(I)            00015200
C                             WFH RTI 9/31/78                           00015210
C                                                                        00015220
      INTEGER  I                                                        00015230
      REAL     C1,C2,C3,K1,K2,K3                                        00015240
      REAL     Y1,Y11                                                   00015250
      REAL  Z(11)                                                       00015260
      DIMENSION YOLD(11)                                                00015270
C                                                                        00015280
C     SAVED OLDIES                                                      00015290
C                                                                        00015300
      XTOP = 2
```

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                XB = 2 * Y(4) - Y(5) - 2 * Y(6) - Y(7) + 2 * Y(8)          00015310
                IF(XB .EQ. 0) RETURN                                        00015320
                XTOP = .7 * (2 * Y(4) + Y(5) - Y(7) - 2 * Y(8))/XB          00015330
                DX = XTOP                                                   00015340
                K1 = DX - 1                                                 00015350
                K2 = DX - 2                                                 00015360
                K3 = DX + 1                                                 00015370
                C1= (DX * (K1) * (K2))/(-6)                                 00015380
                C2= ((K3) * (K1) * (K2))/2                                  00015390
                C3= ((K3) * (DX) * (K2))/(-2)                               00015400
                C4= ((K3) * (DX) * (K1))/6                                  00015410
        C                                                                  00015420
        C        INTERPOLATE                                               00015430
        C                                                                  00015440
                YTOP = Y(5) * C1 + Y(6) * C2 + Y(7) * C3 + Y(8) * C4        00015450
                IS = ISTART - 1                                            00015460
        C   ...   SMOOTH PEAK ALITTLE BEFORE COMPUTING RATE.               00015470
                Z(1)=(Y(1)+.1*Y(2))/1.1                                     00015480
                DO 275 I=2,10                                              00015490
                Z(I)=(Y(I)+.1*(Y(I-1)+Y(I+1)))/1.2                         00015500
        275     CONTINUE                                                   00015510
                Z(11)=(Y(11)+.1*Y(10))/1.1                                 00015520
        C SEE MOD NOTE AT BEGINNING WFH RTI 9/31/78                        00015530
                DO  250 I = IS,8                                           00015540
        250     IF ( Z(I) .EQ. 0 ) Z(I) = 1                                00015550
        C        CALCULATE RATE TO BE AN APPROXIMATION OF                  0001556W
        C                                                                  00015570
        C            INTEGRAL(DY/Y)      ...HIGH RATE FOR SHARP PEAKS.    . 00015580
                RATE = 0                                                   00015590
        C SEE MOD NOTE AT BEGINNING WFH RTI 9/31/78                        00015600
                DO 300 I = ISTART,6                                        00015610
        300     RATE = RATE + (Z(I) - Z(I-1))/Z(I-1)                       00015620
                DO 400 I = 6,7                                             00015630
        400     RATE = RATE + (Z(I) - Z(I+1))/Z(I+1)                       00015640
                RETURN                                                     00015650
                END                                                        00015660
                SUBROUTINE NXTMAX(SPEC,NS,RATEMX,YMAX,NTMAX,SATVAL         00015670
              &   ,SCNDPK,NXTRTE,NSHIFT,IFLAG)                             00015680
        C                                                                  00015690
        C        THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT 00015700
        C        FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND  00015710
        C        GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00015720
        C        (GRANT NGR-05-020-632).1,ID2                              00015730
        C                                                                  00015740
                INTEGER SPEC,SCNDPK,IFLAG(3)                               00015750
                INTEGER RDATE,BITMAP,GCTIME,HIMASS,POINTS,TAPCNT           00015760
                INTEGER NX,NTMAX,IYD,ID1,ID2                               00015770
                DIMENSION SPEC(14,411)                                     00015780
                DIMENSION SCNDPK(3,11),NXTRTE(3)                           00015790
                COMMON PKHIST(20),NPHIST(20)                               00015800
                COMMON YMS(11)                                             00015810
                COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                  00015820
                COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                    00015830
                COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                 00015840
                COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT        00015850
                COMMON /MODES/SGMODE(3),SHMODE(3),GMODE,HMODE              00015860
                COMMON /LFTRIT/ILEFT,IRIGHT                                00015870
                COMMON /MASSES/ISGMAS(3),ISHMAS(3),IGASS,IHMASS            00015880
```

```
      EQUIVALENCE  (YM4,YM5(2))
      EQUIVALENCE  (YM3,YM5(3)),(YM2,YM5(4)),(YM1,YM5(5))
      EQUIVALENCE  (Y0,YM5(6)),(YP1,YM5(7)),(YP2,YM5(8))
      EQUIVALENCE  (YP3,YM5(9)),(YP4,YM5(10)),(YP5,YM5(11))
C
      INTEGER LOCLBG,ILEFT
      REAL NXTRTE,SCAN
      REAL HIST(7),SLOPE,YM5MIN,YP5MIN
      DATA HIST/-.3333,0.,.3333,.6667,1.0,1.3333,1.6667/
C
C     *** ROUTINE TO LOOK AHEAD TO SEE IF THERE ARE ANY OTHER
C     *** SPECTRA IN THE LOCAL REGION OF CURRENT SPECTRUM
C
      I1=NS-13-14*((NS-14)/14)
      I2=NS-12-14*((NS-13)/14)
      I3=NS-11-14*((NS-12)/14)
      I4=NS-10-14*((NS-11)/14)
      I5=NS-9-14*((NS-10)/14)
      I6=NS-8-14*((NS-9)/14)
      I7=NS-7-14*((NS-8)/14)
      I8=NS-6-14*((NS-7)/14)
      I9=NS-5-14*((NS-6)/14)
      I10=NS-4-14*((NS-5)/14)
      I11=NS-3-14*((NS-4)/14)
      I12=NS-2-14*((NS-3)/14)
      I13=NS-1-14*((NS-2)/14)
      I14=NS-14*((NS-1)/14)
C
C TAKE OUT - THIS STATEMENT NO LONGER NECESSARY WITH
C SCAN SUBROUTINE INSERTED.
C                                      WFH RTI 9/31/78
C     DIVISO = HIMASS - LOMASS
      RATEMX=0.0
      NTMAX=0
      NPOS=NSHIFT+1
C     NOW LOOP THROUGH MASSES
C
      DO 60 M=1,411
C
      MI = M + 39
C
C     MI IS THE ACTUAL MASS NUMBER
C
      Y0=SPEC(I8,M)
C THIS MOD MADE AT RTI BECAUSE NO POSSIBLE REASON
C WAS SEEN FOR HAVING AN EQ INSTEAD OF A GE IN
C THIS SITUATION.
C                                      WFH - RTI 6/14/78
      IF(Y0 .GE. SATVAL) GO TO 60
      YM1=SPEC(I7,M)
      IF(Y0 .LE. YM1) GO TO 60
C     PEAK TOP A Y0
      YP1=SPEC(I9,M).
      IF(YP1 .GE. Y0) GO TO 60
C     WE NOW HAVE Y0 AT TOP OF PEAK
40    YM2=SPEC(I6,M)
      YP2=SPEC(I10,M)
      YP3=SPEC(I11,M)
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          YM3=SPEC(I5,M)                                          00016470
          YM4 = SPEC(I4,M)                                        00016480
          YP4=SPEC(I12,M)                                         00016490
          YM5(1)=SPEC(I3,M)                                       00016500
          YY5 = YM5(1)                                            00016510
C         WE HAVE ONLY 14 SPECTRA IN CORE AT A TIME SO:           00016520
C                                                                 00016530
C             NSHIFT   SPECTRA AVAILABLE                          00016540
C                   TO RIGHT OF MODE                              00016550
C                                                                 00016560
C             0              5                                    00016570
C             1              4                                    00016580
C             2                    3                              00016590
          IF(NSHIFT-1) 41,42,43                                   00016600
41        YP5=SPEC(I13,M)                                         00016610
          GO TO 44                                                00016620
42        YP5 = 0.0                                               00016630
          GO TO 44                                                00016640
43        YP4 = 0.0                                               00016650
          YP5 = 0.0                                               00016660
44        CONTINUE                                                00016670
C                                                                 00016680
C         GET HERE TO QUALIFY AS A SINGLET FOR HISTOGRAMMING      00016690
          IF ( YM2 .GE. YM1 ) GO TO 60                            00016700
          IF ( YM3 .GE. YM2 ) GO TO 60                            00016710
          IF ( ILEFT .EQ. 3 ) GO TO 100                           00016720
          IF ( YM4 .GE. YM3 ) GO TO 60                            00016730
100       CONTINUE                                                00016740
          IF ( YP2 .GE. YP1 ) GO TO 60                            00016750
          IF ( YP3 .GE. YP2 ) GO TO 60                            00016760
          IF ( NSHIFT .EQ. 2 ) GO TO 200                          00016770
          IF ( YP4 .GE. YP3 ) GO TO 60                            00016780
200       CONTINUE                                                00016790
C         PUT Y0 AT TOP OF PEAK                                   00016800
          CALL NEWTOP(YM5,RATE,XTOP,YTOP,4)                       00016810
C         CHECK FOR NARROW RISING PEAK (CHAR. OF BACKGROUND) AND. 00016820
C         CHECK FOR PEAK MODE OUT OF BOUNDS. IF SO THE DATA HAD SOME 00016830
C         INFLECTION POINTS.                                      00016840
          YYM5=YTOP - YY5                                         00016850
          IF ( NSHIFT .EQ. 0 ) YX5 = YP5                          00016860
          IF ( NSHIFT .EQ. 1 ) YX5 = YP4                          00016870
          IF ( NSHIFT .EQ. 2 ) YX5 = YP3                          00016880
          YYP5 = YTOP - YX5                                       00016890
          IF ( YYP5 .LT. 30  .AND.  YYM5 .LT. 30 ) GO TO 60       00016900
          IF(XTOP .LE. -1.    .OR.  XTOP .GE. 1.) GO TO 60        00016910
C         CHECK FOR SATURATION                                    00016920
          IF ( YTOP .GE. SATVAL ) GO TO 60                        00016930
          IF ( YM1 .GE. SATVAL ) GO TO 60                         00016940
          IF ( YM2 .GE. SATVAL ) GO TO 60                         00016950
          IF ( YM3 .GE. SATVAL ) GO TO 60                         00016960
          IF ( YM4 .GE. SATVAL ) GO TO 60                         00016970
          IF ( YP1 .GE. SATVAL ) GO TO 60                         00016980
          IF ( YP2 .GE. SATVAL ) GO TO 60                         00016990
          IF ( YP3 .GE. SATVAL ) GO TO 60                         00017000
          IF ( YP4 .GE. SATVAL ) GO TO 60                         00017010
C         SEE IF WE HAVE MAXIMUM RATE                             00017020
          IF ( NSHIFT .GE. 1 ) GO TO 300                          00017030
          SLOPE = (YP5 - YY5)/10.                                 00017040
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          LOCLBG = YY5 + 5 * SLOPE                               00017050
300       CONTINUE                                               00017060
C         TSHIFT = (MI - LOMASS)/DIVISO                          00017070
C THIS SECTION CHANGED TO FUNCTION SUBROUTINE TO                 00017080
C GAIN INSTRUMENT COMPATABILITY.                                 00017090
C                                     UFH RTI 9/31/78            00017100
          TSHIFT=SCAN(MI)                                        00017110
          IF(RATE.LT.RATEMX) GO TO 50                            00017120
          IF((YTOP - YY5) .GE. 160) GO TO 5000                   00017130
          IFLAG(NPOS) = 1                                        00017140
C         FLAG FUNNY MODEL POSSIBLE                              00017150
          GO TO 5500                                             00017160
5000      IFLAG(NPOS) = 0                                        00017170
5500      CONTINUE                                               00017180
C         GET HERE TO QUALIFY AS POSSIBLE MODEL FOR SPECTRUM     00017190
          RATEMX=RATE                                            00017200
C                                                                00017210
C         USE A LINEAR BACKGROUND FIRST CUT APPROXIMATION.       00017220
C                                                                00017230
          MODBKG = SPEC(I1,M)                                    00017240
C         PICK MIN ↑ SPEC(IJ,M) : I1 .LE.  IJ  .LE. I5 @        00017250
          IF ( MODBKG .GT. SPEC(I2,M) ) MODBKG = SPEC(I2,M)      00017260
          IF ( MODBKG .GT. SPEC(I3,M) ) MODBKG = SPEC(I3,M)      00017270
          IF ( MODBKG .GT. SPEC(I4,M) ) MODBKG = SPEC(I4,M)      00017280
          IF ( MODBKG .GT. SPEC(I5,M) ) MODBKG = SPEC(I5,M)      00017290
          IF ( NSHIFT .GE. 1 ) LOCLBG = MODBKG                   00017300
C         USE CONSTANT BACKGROUND IF NO RIGHT END POINT AVAILABLE 00017310
          DO 450 IJ = 1,11                                       00017320
          SCNDPK(NPOS,IJ) = YY5(IJ) - MODBKG                     00017330
450       CONTINUE                                               00017340
          SHMODE(NPOS) = TSHIFT                                  00017350
C                                                                00017360
C         SAVE TSHIFT FOR LATER USE                              00017370
C                                                                00017380
          ISHMAS(NPOS) = MI                                      00017390
C         SAVE MASS OF MODEL PEAK                                00017400
50        CONTINUE                                               00017410
          CONTRI = YTOP - LOCLBG                                 00017420
          IF ( CONTRI .LE. 0 ) GO TO 60                          00017430
          TITTY = TSHIFT + XTOP                                  00017440
          DO 500  I=1,7                                          00017450
          IF (TITTY .LE. HIST(I))  GO TO 600                     00017460
500       CONTINUE                                               00017470
600       CONTINUE                                               00017480
          IH = 7 + I + 3*NSHIFT                                  00017490
C                                                                00017500
C         IH IS IN ONE OF THE THREE SETS  ↑8 TO 140,↑11 TO 170  OR 00017510
C            ,↑14 TO 200                                         00017520
C             AS A FUNCTION OF NSHIFT, NSHIFT = 0, 1 OR 2.       00017530
C                                                                00017540
C         UPDATE HISTOGRAMS                                      00017550
C                                                                00017560
          PKHIST(IH)=PKHIST(IH)+ CONTRI                          00017570
          NPHIST(IH) = NPHIST(IH) + 1                            00017580
C         ....JUST A MINOR VOID ..HUI NENG..                     00017590
60        CONTINUE                                               00017600
C                                                                00017610
C                                                                00017620
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      NXTRTE(NPOS) = RATEMX                                          00017630
C                                                                    00017640
      RETURN                                                         00017650
      END                                                            00017660
      SUBROUTINE OFFSET (G,H,GNU,HNU,GPOS,HPOS)                      00017670
C                                                                    00017680
C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT   00017690
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND      00017700
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00017710
C     (GRANT NGR-05-020-632).                                        00017720
C                                                                    00017730
C                                                                    00017740
C     *** THIS ROUTINE TAKES THE 'GPOS' AND 'HPOS' INFO             00017750
C     *** WHICH CHARACTERIZES WHERE ON THE SPECTRUM SCALE          00017760
C     *** TWO OVERLAPPING COMPONENTS ARE LOCATED WITH              00017770
C     *** RESPECT TO ONE ANOTHER AND MAKES THE NECESSARY           00017780
C     *** DISPLACEMENTS OF THE TWO MODEL PEAKS (ONE FOR            00017790
C     *** EACH OF THE OVERLAPPING COMPONENTS) WITH                 00017800
C     *** RESPECT TO EACH OTHER SO THAT THEY CAN                   00017810
C     *** BE USED BY THE DOUBLET RESOLVING ROUTINE                 00017820
C     *** IN CONJUNCTION WITH THE RAW DATA FOR                     00017830
C     *** THE DOUBLETS THAT HAVE TO BE RESOLVED AND                00017840
C     *** BACKGROUND CORRECTED.                                    00017850
C                                                                    00017860
      DIMENSION G(9),H(11),GNU(18),HNU(18)                           00017870
      INTEGER GPOS,HPOS,HNUT(18),IHSPEC,JLOWER                       00017880
      REAL*8 OFST                                                    00017890
      DATA OFST/'OFFSET'/                                            00017900
C                                                                    00017910
C     ***STRETCH OUT THE MODEL PEAKS A LITTLE                      00017920
C                                                                    00017930
      DO 10 I=1,18                                                   00017940
      GNU(I)=0                                                       00017950
      HNU(I)=0                                                       00017960
10    CONTINUE                                                       00017970
C     PUT G AND H INTO LONGER ARRAYS SO THAT THEY CAN BE ALIGNED TO 00017980
C     SPECTRUM HISTOGRAMIC POSITIONS.                               00017990
      DO 30 I=1,9                                                    00018000
      GNU(I+2) = G(I)                                                00018010
30    CONTINUE                                                       00018020
C     DON'T USE H(1), AND H(11).THESE ARE EXTRA FOR INTERPOLATION   00018030
C     IN LKAHED.                                                    00018040
      DO 110 I=1,9                                                   00018050
      HNUT(I) = H(I+1)                                               00018060
110   CONTINUE                                                       00018070
C                                                                    00018080
C                                                                    00018090
C     ALIGN TO SPECTRUM OF H MODEL                                 00018100
C                                                                    00018110
      IHSPEC = 6 + (HPOS - 1)/3                                      00018120
C                                                                    00018130
C     6 .LE. IHSPEC .LE. 11                                        00018140
C                                                                    00018150
      JLOWER = IHSPEC - 4                                            00018160
      DO 1000 I= 1,9                                                 00018170
      HNU(JLOWER) = HNUT(I)                                          00018180
      JLOWER = JLOWER + 1                                            00018190
1000  CONTINUE                                                       00018200
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C
C      NOW, HNU(IHSPEC) REPRESENTS THE MODE OF THE H-MODEL,  AND          00018210
C      GNU(7) IS THE MODE OF THE G-MODEL                                  00018220
C                                                                         00018230
                                                                          00018240
       RETURN                                                             00018250
       END                                                                00018260
       SUBROUTINE OUTDAT(SRLIB,NNAME)                                     00018270
       INTEGER NNAME(18),MIN,MINI,MAX,MAXI                                00018280
       INTEGER MAD                                                        00018290
       INTEGER PDATE(5),PNAME(32),FLAG                                    00018300
       INTEGER POINTX,TAPCNX,MAXSX                                        00018310
       INTEGER OUTSLT,MAXAMP,EXPNAM,TICRAT                                00018320
       INTEGER NAME,RDATE,BITMAP,GCTIME,LIBMAP,INTEG,LOMASS               00018330
       INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO             00018340
       INTEGER SPEC,IND,IR,BK,NM,NTM                                      00018350
       INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7                   00018360
       INTEGER NUSPEC,NMASS,OVLAP,SRLIB(5)                                00018370
       INTEGER JM(411),JSP(411)                                          00018380
       INTEGER QDUBLT,QSATS,NLINE                                         00018390
       INTEGER NUZEN,IMOLWT                                               00018400
       REAL RMM(411),RMSP(411)                                           00018410
       REAL CLASS(4)/4*' '/,SUBCL(4)/4*' '/                              00018420
       REAL      SPARE5,SPARE6                                            00018430
       REAL*4 TOTION,SIGMA7                                               00018440
       REAL      ISVP8,ISVP9                                              00018450
       REAL    QNORM,ABMAX                                                00018460
       REAL    SATSUM,FORM(5)                                             00018470
       REAL*8 OTDT/' OUTDAT '/,SOURCE/' '/                                00018480
       DIMENSION G(9),H(9),GNU(18),HNU(18)                               00018490
       COMMON PKHIST(20),NPHIST(20)                                       00018500
       COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5                  00018510
       COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                          00018520
       COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                            00018530
       COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                         00018540
       COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT                00018550
       COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                                00018560
       COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS                   00018570
       COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)                00018580
       COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7            00018590
       COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                           00018600
       COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX                00018610
       COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5)         00018620
       COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                            00018630
C      COMMON /SCR/ LIBBLK                                                00018640
       COMMON /ERRORS/ERRMIN,ERRMAX,NERR,SIGERR,IACERR(411)               00018650
       COMMON /PRNTFG/IPFLAG                                              00018660
       COMMON /MASSES/ISGMAS(3),ISHMAS(3),IGMASS,IHMASS                   00018670
       COMMON /DUBBUG/IDEBUG                                              00018680
       COMMON /CHEMPO/QDUBLT,QNORM,QSATS,NLINE                            00018690
       COMMON /IMAD/MAD                                                   00018700
       COMMON /NA/PNAME                                                   00018710
       COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                     00018720
C THESE EQUIVALENCE STMTS. HAVE BEEN FOUND SUPERFLUOUS IN                 00018730
C THE MULTIPLE RUN PROCESSING STRUCTURE OF CLEANUP                        00018740
C AND HAVE BEEN DELETED . THE VARIABLES INSIDE OUTDAT                     00018750
C WERE MODIFIED IN THE FOLLOWING MANNER:                                  00018760
C      EXPID,PDATE,AMP,LOMASX,HIMASX,LSTCNX,GCTIMX,                       00018770
C         INTEGX   -    DELETED FROM OUTDAT                               00018780
                                                                          00018790
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C          SPECNO - INCORPORATED INTO VARIABLE SPCNO              00018800
C          MAXAMP - SHIFTED TO SAVE EXECUTION TIME                00018810
C          TOTION,TICRAT - UNMODIFIED                             00018820
C                             WM F HARGROVE                       00018830
C                               12/6/78                           00018840
C          EQUIVALENCE(EXPID,LIBBLK(84))                          00018850
C          EQUIVALENCE(PDATE,LIBBLK(92))                          00018860
C          EQUIVALENCE (AMP,LIBBLK(257))                          00018870
C          EQUIVALENCE(LOMASX,LIBBLK(75))                         00018880
C          EQUIVALENCE(HIMASX,LIBBLK(74))                         00018890
C          EQUIVALENCE(SPECNO,LIBBLK(78))                         00018900
C          EQUIVALENCE(MAXAMP,LIBBLK(77))                         00018910
C          EQUIVALENCE(TOTION,LIBBLK(1))                          00018920
C          EQUIVALENCE(LSTCNX,LIBBLK(70))                         00018930
C          EQUIVALENCE(GCTIMX,LIBBLK(90))                         00018940
C          EQUIVALENCE(INTEGX,LIBBLK(89))                         00018950
C          EQUIVALENCE(ABMAX,LIBBLK(49))                          00018960
C          EQUIVALENCE(TICRAT,LIBBLK(72))                         00018970
           DATA HOW/1H /                                          00018980
C     *****************HERE WE GO****************************      00018990
C     TAPCNT 1000 IF WE ARE GOING TO WRITE THE BIT MAP            00019000
           IF ( TAPCNT .EQ. 1000 ) GO TO 12                       00019010
C THIS MOD INSERTED  TO WEED OUT ELLUTANTS WHICH HAVE NO          00019020
C SUITABLE MODEL.....                                             00019030
C                           RTI WFH 11/21/78                      00019040
           IF(IGMASS.GT.0)GO TO 91                                00019050
           IF(IDEBUG.NE.0)WRITE(IPTR2,3334)                       00019060
     3334 FORMAT(1X,' SPECTRUM REJECTED FOR LACK OF SUITABLE MODEL')  00019070
           RETURN                                                 00019080
C                                                                 00019090
      91 ISWEAK = IGMASS - 39                                     00019100
           IF ( NUSPEC(ISWEAK) .GT. 0 ) GO TO 93                  00019110
           IF ( IDEBUG .EQ. 0 ) GO TO 92                          00019120
           INEWM=IGMASS-MAD                                       00019130
C          CALL TRACE(IGMASS,MAD)                                 00019140
C THIS WRITE STMT HAS BEEN MADE CONDITIONAL TO SAVE PAPER         00019150
C                           WFH RTI 9/31/78                       00019160
           IF(IDEBUG.EQ.0)GO TO 92                                00019170
           WRITE(IPTR2,3333) INEWM                                00019180
      92   RETURN                                                 00019190
      93   CONTINUE                                               00019200
C          CALL ZERO(LIBBLK,1024)                                 00019210
C SEE COMMENT AT TOP                                              00019220
C                           WFH - RTI 12/6/78                     00019230
C          DO 30 I=1,1024                                         00019240
C30        LIBBLK(I)=0                                            00019250
           TOTION=0.0                                             00019260
C          CALL TRACE(NMASS)                                      00019270
           DO 4  I = 1,NMASS                                      00019280
      4    IF  ( NUSPEC(I) .LT. 0 ) NUSPEC(I) = 0                 00019290
           SATSUM = 0                                             00019300
           DO 5  I = 1,NMASS  .                                   00019310
           NUZEN = NUSPEC(I)                                      00019320
           IF ( NUZEN .GE. SATVAL ) SATSUM = SATSUM + NUZEN       00019330
      5    TOTION = TOTION + NUZEN                                00019340
C           REJECT SPECTRUM IF TOTION IS LESS THAN MINIMUM TIC    00019350
           IF ( TOTION  .LT.  MINTIC ) RETURN                     00019360
C           TICRAT IS CLEANUP RATIO                               00019370
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         SIGMA7 = SIGMA7 - QSATS * SATVAL + SATSUM          00019380
C        SINCE COMPUTED SATURATED VALUES MAY CAUSE THE CLEANED UP      00019390
C        TIC TO EXCEED THE RAW, WE SUBSTITUTE CALCULATED VALUES        00019400
C        FOR MAXIMUM VALUES. THIS IS A LIMIT OF OUR 16 BIT INTEGER,    00019410
C        AND 24570 SATURATED DEFAULT VALUE IN OUR GC COLLECTION        00019420
C        PHASE.                                             00019430
         IF ( TOTION .GE. SIGMA7 ) TOTION = SIGMA7 - 1      00019440
         TICRAT=TOTION*100.0/SIGMA7                         00019450
         IF ( IDEBUG .EQ. 0 ) GO TO 6                       00019460
         WRITE(IPTR2,1000) TOTION,SIGMA7,TICRAT,SATSUM      00019470
6        OUTSLT=0                                           00019480
         LSTCNT=LSTCNT+1                                    00019490
C        CALL MOVE(EXPNAM,EXPID,5)                          00019500
C SEE COMMENT AT TOP                                        00019510
C                        WFH - RTI 12/6/78                  00019520
C        DO 39 I=1,5                                        00019530
C39      EXPID(I)=EXPNAM(I)                                 00019540
C        CALL MOVE(NAME,PNAME,32)                           00019550
C THIS LOOP COMENTED OUT TO SUIT WATFIV AND BECAUSE IT SERVES 00019560
C NO APPARENT PURPOSE...                                    00019570
C                        WFH AT RTI 4/25/78                 00019580
C        DO 32 I=1,32                                       00019590
C 32     PNAME(I)=NAME(I)                                   00019600
C SEE COMMENT AT TOP                                        00019610
C                        WFH - RTI 12/6/78                  00019620
C        INTEGX=INTEG                                       00019630
C        CALL MOVE(RDATE,PDATE,5)                           00019640
C  SEE COMMENT AT TOP                                       00019650
C                        WFH - RTI 12/6/78                  00019660
C        DO 31 I=1,5                                        00019670
C31      PDATE(I)=RDATE(I)                                  00019680
C        LOMASX=LOMASS                                      00019690
C        HIMASX=HIMASS                                      00019700
C        LSTCNX=LSTCNT                                      00019710
C        SPECNO=SPCNO                                       00019720
C        CALL TRACE(NMASS)                                  00019730
C        MAXAMP DETERMINATION SHIFTED ...                   00019740
C                        WFH - RTI 12/6/78                  00019750
         IF ( IPFLAG .EQ. 0 ) GO TO 12                      00019760
         MAXAMP=0                                           00019770
         DO 10 I=1,NMASS                                    00019780
 10      IF(MAXAMP.LT.NUSPEC(I)) MAXAMP=NUSPEC(I)           00019790
C        COMPUTE ABSOLUTE MAXIMUM AMPLITUDE.                00019800
         ABMAX = MAXAMP/QNORM                               00019810
         CALL KAPUT( SPCNO,TOTION,TICRAT,ABMAX )            00019820
C        THE ABOVE PRINTS OUT THE "CHEMISTS" MINIMUM STUFF. 00019830
11       CONTINUE                                           00019840
C        CALL SETMAS(LIBMAP,LSTCNT)                         00019850
C...     CALL PUTFIL(OUTSLT,LIBBLK,LSTCNT)                  00019860
C14      CALL CHKFIL(OUTSLT,FLAG)                           00019870
C....    IF(FLAG) 13,14,15                                  00019880
C..15    CONTINUE                                           00019890
C        WRITE(IPTR3,34) (LIBBLK(I),I=1,128)                00019900
C 34 FORMAT(3(/3214)/1314,10A4,914/)                        00019910
         IZ=0                                               00019920
         DO 81 I=1,411                                      00019930
         IF(NUSPEC(I).LE.0)GO TO 81                         00019940
         IZ=IZ+1                                            00019950
```

```
      JM(IZ)=I+39-MAD                                          00019960
C     MM(IZ)=(I+39-MAD)*10                                     00019970
      RMM(IZ)=I+39-MAD                                         00019980
      JSP(IZ)=NUSPEC(I)                                        00019990
C     MSP(IZ)=NUSPEC(I)                                        00020000
      RMSP(IZ)=NUSPEC(I)                                       00020010
81    CONTINUE                                                 00020020
C THESE WRITE STMTS HAVE BEEN MADE CONDITIONAL FOR CONSISTENCY 00020030
C                                        WFH RTI 9/31/78       00020040
      IF(IDEBUG.EQ.0)GO TO 85                                  00020050
      WRITE(IPTR2,80)SPCNO,IZ,(NNAME(K),K=1,15)                00020060
80    FORMAT(4X,'SPECTRA = ',I5,'  NO. OF PEAKS = ',I4,2X,15A4,' CLEANE 00020070
     *D.'/)                                                    00020080
      WRITE(IPTR2,83)(JM(K),JSP(K),K=1,IZ)                     00020090
83    FORMAT(46(1816/)/)                                       00020100
85    CALL XTREM(JSP,IZ,MIN,MINI,MAX,MAXI)                     00020110
      BASE=MAX                                                 00020120
C     CALL TRACE(IZ)                                           00020130
      DO 60 I=1,IZ                                             00020140
60    RMSP(I)=(RMSP(I)/BASE)*100.                              00020150
      RMSP(MAXI)=99.99                                         00020160
C     WRITE(8,600)SPECNO,IZ,(NNAME(I),I=1,15),CLASS,SUBCL,HOW,IMOLWT 00020170
C THE FOLLOWING TWO WRITE STATEMENTS WERE COMENTED OUT BECAUSE 00020180
C THEY SEEM TO YEILD NOTHING INTERESTING AND ALSO BECAUSE NO   00020190
C CARRIAGE CONTROL FOR THE PRINTER HAS BEEN INCLUDED           00020200
C                                        WM.F.HARGROVE - RTI   00020210
C     WRITE(IPTR2,600)SPECNO,IZ,(NNAME(I),I=1,15),CLASS,SUBCL,HOW,IMOLWT00020220
C600   FORMAT(I5,I3,15A4,9A1,I3)                               00020230
C                                                              00020240
C HERE IS THE MAIN OUTPUT STATEMENT WRITING THE CLEANUPED      00020250
C UP SPECTRUM TO A DISK DATASET                                00020260
C THE CHANGE TO A SUBROUTINE CALL HAS BEEN MADE WITH THE       00020270
C ONSET OF MULTIPLE RUN PROCESSING AND A LINEAR SYSTEM.        00020280
C                                        WM F HARGROVE         00020290
C                                        11/29/78              00020300
C     WRITE(9) SPCNO,NUSPEC                                    00020310
      CALL WRTSPC(SPCNO,NUSPEC,QDUBLT,TICRAT,IZ,TOTION)        00020320
      N=(IZ+7)/8                                               00020330
      IF=1                                                     00020340
      IT=8                                                     00020350
      DO 62 I=1,N                                              00020360
C THIS MOD INSERTED TO BLOT OUT APPARENTLY USELESS WRITE STMT. 00020370
C                         WFH - 5/31/78 - RTI                  00020380
C     WRITE(8,601)(RMM(K),RMSP(K),K=IF,IT)                     00020390
C ANOTHER WRITE STMT MADE CONDITIONAL FOR CONSISTENCY'S SAKE   00020400
C                                        WFH RTI 9/31/78       00020410
      IF(IDEBUG.EQ.0)GO TO 63                                  00020420
      WRITE(IPTR2,602)(RMM(K),RMSP(K),K=IF,IT)                 00020430
63    CONTINUE                                                 00020440
      IF=IT+1                                                  00020450
62    IT=IF+7                                                  00020460
C601   FORMAT(8(F5.1,F5.2)),                                   00020470
602   FORMAT(1X,8(F5.1,F5.2))                                  00020480
      DO 61 I=1,411                                            00020490
      RMM(I)=0.0                                               00020500
61    RMSP(I)=0.0                                              00020510
C     BASM=MM(MAXI)/10                                         00020520
C     BASE=MAX                                                 00020530
```

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C         DO 50 I=1,IZ
C         HD1=JSP(I)                                              00020540
C     50  MSP(I)=(HD1/BASE)*10000                                 00020550
C....                                                             00020560
C.....                                                            00020570
C         WRITE(8)MW,II,IZ,BASM,NNAME,SOURCE,FORM,(MM(K),MSP(K),K=1,IZ)  00020580
12        CONTINUE                                                00020590
C         DON'T WRITE BITMAP UNTIL LAST RECORD.                   00020600
C         RETURN                                                  00020610
C         HERE FOR WRITING BITMAP TO LIST.MAS                     00020620
C..12     CALL ZERO(LIBBLK,1024)                                  00020630
C     12  DO 33 I=1,1024                                          00020640
C     33  LIABLK(I)=0                                             00020650
C         OUTSLT = 0                                              00020660
C         LSTCNX=LSTCNT                                           00020670
C         READ(7,20)LIBBLK                                        00020680
C     20  FORMAT(I8)                                              00020690
C         CALL GETFIL(OUTSLT,LIBBLK,0)                            00020700
C..20     CALL CHKFIL(OUTSLT,FLAG)                                00020710
C         IF(FLAG) 13,20,21                                       00020720
C..21     CONTINUE                                                00020730
C..       CALL MOVE(LIBMAP,LIBBLK,17)                             00020740
C         DO 35 I=1,17                                            00020750
C     35  LIBBLK(I)=LIBMAP(I)                                     00020760
C         WRITE(IPTR3,36)LIBBLK                                   00020770
C     36  FORMAT(I8)                                              00020780
C..       CALL PUTFIL(OUTSLT,LIBBLK,0)                            00020790
C..16     CALL CHKFIL(OUTSLT,FLAG)                                00020800
C..       IF(FLAG) 13,16,17                                       00020810
C..13     CALL PUTNUM('FILE ERROR FLAG = ',FLAG)                  00020820
C..       CALL PUTSTR('BOMBED WRITTING TO LIST.MAS IN OUTDAT')    00020830
C..       STOP                                                    00020840
C..17     CALL CLSFIL(OUTSLT)                                     00020850
          RETURN                                                  00020860
1000      FORMAT(/,' TOTAL ION CURRENT =',F8.0,/,' UNC SIG =',E15.8,  00020870
         -/' TICRAT =',I3/' SAT PEAK SUM =',F12.0//)              00020880
3333      FORMAT(/,' SPECTRUM REJECTED BECAUSE MASS ',I3,',THE ',  00020890
         1' MODEL PEAK, HAS 0 CONTRIBUTION      '/)               00020900
          END                                                     00020910
          SUBROUTINE PARDIR                                       00020920
C                                                                 00020930
C         THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT  00020940
C         FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND     00020950
C         GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  00020960
C         (GRANT NGR-05-020-632).                                 00020970
C FURTHER NOTE:                                                   00020980
C THIS VERSION OF PARDIR HAS BEEN COMPLETELY REWRITTEN IN ORDER TO ALLOW  00020990
C FOR PROCESSING OF MULTIPLE RUNS. THIS VERSION OF PARDIR IS ALSO USED    00021000
C IN THE VERSIN OF CLEANUP SUPPLIED TO EPA BY RTI.THE FUNCTION OF   00021010
C PARDIR IS TO READ IN CONTROL PARAMETERS FROM A TERMINAL OR       00021020
C CONTROL CARDS THAT ARE CONSTANT ACROSS DIFFERENT RUNS. THE       00021030
C MEANING OF THE VARIABLES READ HEREIN SHOULD BE SELF-DOCUMENTING  00021040
C FROM THE ECHO MESSAGES.                                         00021050
C                                 WM.F.HARGROVE                    00021060
C                                 RTI 11/22/78                     00021070
C                                                                 00021080
C                                                                 00021090
          COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT          00021100
          INTEGER IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                 00021110
```

```
      COMMON /TOMS/ITOM                                           00021120
      COMMON /PRNTFG/IPFLAG                                       00021130
      COMMON /LFTRIT/ILEFT,IRIGHT                                 00021140
      COMMON /CRATMX/RATMXX                                       00021150
      COMMON /DUBBUG/IDEBUG                                       00021160
      COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                     00021170
      COMMON /AVG/ NAVG,HAVG                                      00021180
      INTEGER ITOM,IPFLAG,ILEFT,IRIGHT,IDEBUG,NTHIRD             00021190
      REAL RATMXX,RATM                                            00021200
      INTEGER NAVG,HAVG                                           00021210
      INTEGER MINNY,MINTIC                                        00021220
C PROMPT AND READ CONTROL PARMS - LIFTED FROM OLD CLEANUP SOURCE 00021230
C AN ADDITIONAL PARAMETER WAS ADDED TO AVERAGE N INPUT           00021240
C SPECTRA IF IT BECAME NECESSARY - AS WITH THE INCOS DATA        00021250
C                                       RTI - WFH 1/14/79        00021260
      WRITE(IPTR1,3240)                                          00021270
 3240 FORMAT(1X,'ENTER CLEANUP PRINT FLAG(IN I1):')              00021280
      READ(IRDR,3241) IPFLAG                                     00021290
 3241 FORMAT(I1)                                                 00021300
      WRITE(IPTR1,3242) IPFLAG                                   00021310
 3242 FORMAT(1X,'IPFLAG=',I1)                                    00021320
C                                                                00021330
C         IPFLAG IS PRINT OPTION FLAG FOR CLEANUP                00021340
C         INITIALIZE DEFAULTS FOR VARIOUS PARAMETERS IN COMMON   00021350
      WRITE(IPTR1,3100)                                          00021360
 3100 FORMAT(1X,'ENTER DEBUGGING SWITCH IN I1 (0=N,1=Y):')       00021370
      READ(IRDR,3101) IDEBUG                                     00021380
 3101 FORMAT(I1)                                                 00021390
      WRITE(IPTR1,3103) IDEBUG                                   00021400
 3103 FORMAT(1X,'IDEBUG=',I1)                                    00021410
C                                                                00021420
      WRITE(IPTR1,123)                                           00021430
  123 FORMAT(1X,'ENTER # OF INPUT SPECTRA TO AVERAGE IN I2:')    00021440
      READ(IRDR,121) NAVG                                        00021450
  121 FORMAT(I2)                                                 0002146W
      WRITE(IPTR1,122) NAVG                                      00021470
  122 FORMAT(1X,'NAVG=',I2)                                      00021480
      HAVG=NAVG/2+1                                              00021490
      WRITE(IPTR1,3120)                                          00021500
 3120 FORMAT(1X,'MINIMUM THIRDS BETWEEN ELLUANTS IN I1:')        00021510
      READ(IRDR,3121) NTHIRD                                     00021520
 3121 FORMAT(I1)                                                 00021530
      WRITE(IPTR1,3123) NTHIRD                                   00021540
 3123 FORMAT(1X,'THIRDS BETWEEN ELLUANTS=',I1)                   00021550
C                                                                00021560
      WRITE(IPTR1,3130)                                          00021570
 3130 FORMAT(1X,'ENTER DETECTION WINDOW IN I4:')                 00021580
      READ(IRDR,3131) ITOM                                       00021590
 3131 FORMAT(I4)                                                 00021600
      WRITE(IPTR1,3132) ITOM                                     00021610
 3132 FORMAT(1X,'DETECTION WINDOW=',I4)                          00021620
C                               .                                00021630
      WRITE(IPTR1,3140)                                          00021640
 3140 FORMAT(1X,'ENTER MINIMUM FOR LT 5 PEAKS IN I6:')           00021650
      READ(IRDR,3141) MINNY                                      00021660
 3141 FORMAT(I6)                                                 00021670
      WRITE(IPTR1,3143) MINNY                                    00021680
 3143 FORMAT(1X,'MINNY=',I6)                                     00021690
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C                                                                    00021700
      WRITE(IPTR1,3150)                                              00021710
 3150 FORMAT(1X,'ENTER MINIMUM FOR MORE THAN 4 PEAKS IN I6:')        00021720
      READ(IRDR,3151) MINTIC                                         00021730
 3151 FORMAT(I6)                                                     00021740
      WRITE(IPTR1,3152) MINTIC                                       00021750
 3152 FORMAT(1X,'MINTIC=',I6)                                        00021760
C                                                                    00021770
      WRITE(IPTR1,3160)                                              00021780
 3160 FORMAT(1X,'ENTER MINIMUM QUALIFYING RATE IN F8.4:')           00021790
      READ(IRDR,3161) RATM                                          00021800
 3161 FORMAT(F8.4)                                                   00021810
      WRITE(IPTR1,3162) RATM                                        00021820
 3162 FORMAT(1X,'RATM=',F8.4)                                        00021830
C                                                                    00021840
      WRITE(IPTR1,3170)                                              00021850
 3170 FORMAT(1X,'ENTER ERROR RATIO IN F8.4:')                        00021860
      READ(IRDR,3171) RATMXX                                         00021870
 3171 FORMAT(F8.4)                                                   00021880
      WRITE(IPTR1,3172) RATMXX                                       00021890
 3172 FORMAT(1X,'RATMXX=',F8.4)                                      00021900
C                                                                    00021910
      WRITE(IPTR1,3180)                                              00021920
 3180 FORMAT(1X,'ENTER POINTS TO LEFT OF MODE IN I3:')               00021930
      READ(IRDR,3181) ILEFT                                          00021940
 3181 FORMAT(I3)                                                     00021950
      WRITE(IPTR1,3182) ILEFT                                        00021960
 3182 FORMAT(1X,'ILEFT=',I3)                                         00021970
C                                                                    00021980
      WRITE(IPTR1,3190)                                              00021990
 3190 FORMAT(1X,'ENTER POINTS TO RIGHT OF MODE IN I3:')              00022000
      READ(IRDR,3191) IRIGHT                                         00022010
 3191 FORMAT(I3)                                                     00022020
      WRITE(IPTR1,3192) IRIGHT                                       00022030
 3192 FORMAT(1X,'IRIGHT= ',I3)                                       00022040
      RETURN                                                         00022050
      END                                                            00022060
      SUBROUTINE SATLSQ (NS,M,RPKHGT,G,SPEC,SATVAL,GPOS,OVLAP,HPOS,PKHIS00022070
     *T)                                                             00022080
C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT   00022090
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND      00022100
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00022110
C     (GRANT NGR-05-020-632).                                        00022120
C                                                                    00022130
C                                                                    00022140
C     THIS ROUTINE COMPUTES SATURATED VALUES IN THE                  00022150
C     FOLLOWING WAY:                                                 00022160
C                                                                    00022170
C       1. REMOVE LOCAL BACKGROUND FROM SATURATED PROFILE.           00022180
C                                                                    00022190
C       2. COMPUTE THE RATIOS OF PEAK(I)/MODEL(I)                    00022200
C          FOR NON-SATURATED POINTS IN THE PEAK.                     00022210
C                                                                    00022220
C       3. GET THE AVERAGE RATIO, AND MULTIPLY IT TIMES             00022230
C          THE MODEL MODE. THIS IS THE RETURNED SATURATED            00022240
C          VALUE.                                                    00022250
      REAL    LOCLBG,GG,PKHIST(20)                                   00022260
      INTEGER SPEC(14,411),GPOS,OVLAP,HPOS                           00022270
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          INTEGER MINHGT,SATLST,SATINX                           00022280
          INTEGER IJ,IK,IL,LSTOP,RSTART,STOPF,RCOUNT             00022290
          DIMENSION G(9),Y(13),RATIOS(13)                        00022300
          COMMON /CSATLS/SATLST(25),SATINX                       00022310
          COMMON /MODES/SGMODE(3),SHMODE(3),GMODE,HMODE          00022320
          COMMON /QUIXOT/IQUIT                                   00022330
C         I2=NS-12-14*((NS-13)/14)                               00022340
C         I3=NS-11-14*((NS-12)/14)                               00022350
C         I4=NS-10-14*((NS-11)/14)                               00022360
C         I5=NS-9-14*((NS-10)/14)                                00022370
C         I6=NS-8-14*((NS-9)/14)                                 00022380
C         I7=NS-7-14*((NS-8)/14)                                 00022390
C         I8=NS-6-14*((NS-7)/14)                                 00022400
C         I9=NS-5-14*((NS-6)/14)                                 00022410
C         I10=NS-4-14*((NS-5)/14)                                00022420
C         I11=NS-3-14*((NS-4)/14)                                00022430
C         I12=NS-2-14*((NS-3)/14)                                00022440
C         I13=NS-1-14*((NS-2)/14)                                00022450
          IK = 13                                                00022460
          DO 5    I = 1,12                                       00022470
          IL = IK - 1                                            00022480
          IJ = NS - IL - 14 * ((NS - IK)/14)                     00022490
          Y(I) = SPEC(IJ,M)                                      00022500
          IK = IK - 1                                            00022510
5         CONTINUE                                               00022520
C         SATVAL WILL BE DEFAULT IN CASE OF SUPER SATURATION     00022530
          RPKHGT = -SATVAL                                       00022540
          MINHGT = .05 * SATVAL                                  00022550
C         MINHGT IS MINIMUM ACCEPTABLE HEIGHT IN MODEL FOR RATIOING. 00022560
          ILFT = 0                                               00022570
          ILEFT = 0                                              00022580
          IRIGHT = 0                                             00022590
          NPTS = 12                                              00022600
          NSATS = 0                                              00022610
          DO  50 I = 1,NPTS                                      00022620
          IF (Y(I).GE.SATVAL) GO TO   10                         00022630
          IF (ILFT.EQ.1) GO TO  20                               00022640
C                                                                00022650
C         COUNT POINTS TO LEFT OF FIRST SATURATED POINT          00022660
C                                                                00022670
          ILEFT = ILEFT + 1                                      00022680
          GO TO  50                                              00022690
20        CONTINUE                                               00022700
C         COUNT POINTS TO RIGHT OF LAST SATURATED POINT          00022710
          IRIGHT = IRIGHT + 1                                    00022720
          GO TO  50                                              00022730
C         FOUND FIRST SATURATED POINT                            00022740
10        ILFT = 1                                               00022750
          NSATS = NSATS + 1                                      00022760
C         NSATS COUNTS SATURATED VALUES.                         00022770
50        CONTINUE                                               00022780
C         ILEFT = NUMBER OF POINTS TO LEFT OF FIRST SATURATED POINT.  00022790
C         IRIGHT = NUMBER OF POINTS TO RIGHT OF LAST SATURATED POINT. 00022800
C         FIND MIDDLE POINT OF SATURATED VALUES AND D MAKE SURE  00022810
C         7 IS IN +MID-1,MID+10.NOTE:THE INTERVAL IS CLOSED.     00022820
          IQUIT = 0                                              00022830
          IFIRST = ILEFT + 1                                     00022840
          ILAST = ILEFT + NSATS                                  00022850
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C                                                                    00022860
C                                                                    00022870
C        LLLLLSSSSRRR                                             00022880
C                                                                    00022890
C        IFIRST ILAST                                                00022900
C                                                                    00022910
C        RMID IS MIDDLE POINT OF SATURATED VALUES, AND REAL.        00022920
         RMID = ( IFIRST + ILAST )/2.0                               00022930
         RWIND = 7.0 - RMID                                          00022940
C        NOTE: 7 IS INDEX OF CURRENT SPECTRUM.                       00022950
C        7 MUST BE WITHIN (RMID-1,RMID+1).                           00022960
C                                                                    00022970
C        ACTUALLY, RMID MUST BE IN +6,80 FOR SATURATED              00022980
C        VALUE TO BE PROCESSED.                                      00022990
         IF ( RWIND .LT. 0 ) RWIND = -RWIND                          00023000
         IF ( RWIND .LE. 1.0 ) GO TO 60                              00023010
         IQUIT = 1                                                   00023020
         RETURN                                                      00023030
60       CONTINUE                                                    00023040
C        PRINT SATURATED MASS ENCOUNTERED STUFF                      00023050
         MASS = M + 39                                               00023060
C        SEE IF MASS BELONGS TO PREDESSOR.                           00023070
         DO 62 I = 1,SATINX                                       -  00023080
         IF ( SATLST(I) .NE. MASS ) GO TO 62                         00023090
         SATLST(I) = 0                                               00023100
         IQUIT = 2                                                   00023110
         RETURN                                                      00023120
62       CONTINUE                                                    00023130
C        DETERMINE IF THIS MASS BELONGS TO AN AJACENT SPECTRUM       00023140
         IF ( OVLAP .EQ. 0 )  GO TO 70                               00023150
         NXTSPC = 6 + ( HPOS-1 )/3                                   00023160
C        SEE IF SATVALS OCCUR IN NEXT SPECTRUM CONTINUOUSLY          00023170
         IF ( ILAST .LT. NXTSPC ) GO TO 70                           00023180
         RDIFF = NXTSPC - RMID                                       00023190
C        SEE IF RMID IS CLOSE TO NEXT SPECTRUM.                      00023200
         IF ( RDIFF .GT. 1 ) GO TO 70                                00023210
C        GIVE UNDECIDED MASS TO SPECTRUM WITH BIGGEST TIC.           00023220
         IF ( PKHIST(GPOS) .GE. PKHIST(HPOS) ) GO TO 65              00023230
         IQUIT = 1                                                   00023240
         RETURN                                                      00023250
65       CONTINUE                                                    00023260
C        FLAG FOR NEXT GUY TO AVOID.                                 00023270
         SATLST(SATINX) = MASS                                       00023280
         SATINX = SATINX + 1                                         00023290
         IF ( SATINX .EQ. 26 ) SATINX = 25                           00023300
70       CONTINUE                                                    00023310
C THE LAST THREE ARGUMENTS Y,Y,Y) HAVE BEEN CHANGED TO              00023320
C SATVAL,SATVAL,SATVAL) TO SUIT WATFIV...THEY HAVE NO               00023330
C FUNCTION WITHIN SPEPRT.                                            00023340
C                              WFH RTI 4/30/78                       00023350
         CALL SPEPRT(1,MASS,Y,SATVAL,SATVAL,SATVAL)                  00023360
C THE LAST TWO ARGUMENTS Y,Y) HAVE ALSO BEEN CHANGED TO SATVAL,SATVAL) 00023370
C TO SUIT WATFIV. ... THEY HAVE NO APPARENT FUNCTION INSIDE SPEPRT  00023380
C                              WFH RTI 4/30/78                       00023390
C        PRINT DEFAULT SATURATED VALUE                               00023400
         CALL SPEPRT(2,NPTS,Y,SATVAL,SATVAL,SATVAL)                  00023410
C        ******* NOW BEGIN OUR SATURATION STUFF **********          00023420
         LSTOP = ILEFT                                               00023430
         RSTART = NPTS - IRIGHT + 1
```

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        LOCLBG = Y(I)
C         SUBTRACT LEFT POINT FROM ALL VALUES AS AN APPROXIMATION
C       OF BACKGROUND.THIS IS TO BE SYMMETRIC WITH MODEL PEAK.
        STOPF = 0
        IF ( LSTOP .NE. 0) GO TO 90
        STOPF = 1
        GO TO 105
90      CONTINUE
        DO 100 I = 1,LSTOP
100     Y(I) = Y(I) - LOCLBG
105     CONTINUE
        IF (STOPF .EQ. 1 .AND. RSTART .GT. NPTS) GO TO 900
C       IF WE GO TO 900 IT MEANS ALL VALUES ARE SATURATED
        IF (RSTART .GT. NPTS) GO TO 120
        DO 110 I = RSTART,NPTS
110     Y(I) = Y(I) - LOCLBG
120     CONTINUE
        RATO = 0
        RCOUNT = 0
        IF (LSTOP .LT. 3) GO TO 300
        DO 200 I = 3,LSTOP
        GG = G(I-2)
        IF( GG .LT. MINHGT ) GO TO 200
C       NOTE: MINGHT > 0
        RATIOS(I) = Y(I)/GG
        RATO = RATO + RATIOS(I)
        RCOUNT = RCOUNT + 1
200     CONTINUE
300     CONTINUE
        IF (RSTART .GT. 11) GO TO 350
        DO 325 I = RSTART,11
        GG = G(I-2)
        IF ( GG .LT. MINHGT ) GO TO 325
        RATIOS(I) = Y(I)/GG
        RATO = RATO + RATIOS(I)
        RCOUNT = RCOUNT + 1
325     CONTINUE
350     CONTINUE
        IF(RCOUNT .LE. 1) GO TO 900
C       ABOVE TAKES CARE OF SUPER SATURATION
        RATO = RATO/RCOUNT
        IF(RATO .LE. 0) GO TO 900
C       THE ABOVE TAKES CARE OF A VERY FUNNY LOCAL BACKGROUND
        RPKHGT = RATO * G(5)
C       THE ABOVE TAKES CARE OF SATURATED PEAKS WITH TO HIGH
C       OF BACKGROUND APPROXIMATIONS.
        CALL SPEPRT(3,I,RPKHGT,LOCLBG,RATO,G(5))
        RETURN
900     CONTINUE
        CALL SPEPRT(4,I,RPKHGT,RATO,RATO,RATO)
        RETURN
        END
C
C THIS SUBROUTINE WAS INCORPORATED TO ACCOUNT FOR THE POSSIBILITY
C OF DIFFERENT SCAN FUNCTIONS ON THE FINNIGAN QUADROPOLE
C SPECTROMETER AND TO ALLOW FOR MAGNETIC INSTRUMENTS IN THE FUTURE
C                                         WFH RTI 9/31/78
C
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      REAL FUNCTION SCAN(MASS)                                     00024030
      INTEGER*4 MASS                                               00024040
      REAL*4 HIMASS/450./,LOMASS/40./                              00024050
C                                                                  00024060
      RMASS=MASS                                                   00024070
      SCAN=(RMASS-LOMASS)/(HIMASS-LOMASS)                          00024080
      RETURN                                                       00024090
      END                                                          00024100
      SUBROUTINE SETBUG(NNAME,EOF)                                 00024110
C                                                                  00024120
      INTEGER CLNFLG                                               00024130
C     THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT 00024140
C     FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND    00024150
C     GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00024160
C     (GRANT NGR-05-020-632).                                      00024170
C                                                                  00024180
C FURTHER NOTE:                                                    00024190
C THIS VERSION OF SUBROUTINE SETBUG HAS REWRITTEN IN ORDER TO PERMIT 00024200
C MULTIPLE RUN PROCESSING AND TO FIT INTO THE CONTEXT OF THE EPA AND 00024210
C RTI ACQUISITION SYSTEMS. ITS FUNCTION IS TO READ AND FILL THE SPECTRUM 00024220
C BUFFER WITH THE FIRST 13 SPECTRA FROM EACH RUN.                  00024230
      COMMON PKHIST(20),NPHIST(20)                                 00024240
      COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5            00024250
      COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                    00024260
      COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                      00024270
      COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                   00024280
      COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT          00024290
      COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                          00024300
      COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS             00024310
      COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)          00024320
      COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7      00024330
      COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                     00024340
      COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX          00024350
      COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5)   00024360
      REAL SATVAL                                                  00024370
      INTEGER AVGSPC(411),NAVG,HAVG                                00024380
      INTEGER EOF,LIBBLK,RDATE,LOMASS,HIMASS,ADS,POINTS,           00024390
     1SPCNO,SPEC,NNAME(18)                                         00024400
      COMMON /SCR/ LIBBLK(1024)                                    00024410
      COMMON /IADS/ ADS                                            00024420
      COMMON /IMAD/ MAD                                            00024430
      COMMON /AVG/ NAVG,HAVG                                       00024440
C READ IN RUN HEADER AND RETURN IF END OF FILE                    00024450
      CALL OPNRUN(LIBBLK,EOF)                                      00024460
      IF(EOF.NE.0)RETURN                                           00024470
C HOUSE CLEANING FOR HISTORICAL VARIABLES STILL LEFT IN CLEANUP   00024480
      NMASS=411                                                    00024490
      DO 10 I=1,2                                                  00024500
   10 RDATE(I)=LIBBLK(I+27)                                        00024510
C SETTING OF HIGH MASS, LOMASS AND OF # OF SPECTRA IN RUN         00024520
      MAXSP=LIBBLK(38)                                             00024530
      LOMASS=40                                                    00024540
      HIMASS=450                                                   00024550
      ADS=LIBBLK(36)                                               00024560
      MAD=40-LOMASS                                                00024570
      POINTS=40                                                    00024580
C BY SERENDIPIDY NNAME CAN BE MODIFIED TO CONTAIN THE RUN TITLE AND 00024590
C EXPNAM TO CONTAIN THE INSTRUMENT TYPE...                        00024600
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          DO 20 I=1,18                                                 00024610
       20 NNAME(I)=LIBBLK(12+I)                                        00024620
          DO 30 I=1,5                                                   00024630
       30 EXPNAM(I)=LIBBLK(7+I)                                        00024640
C THE INTERNALS OF SETBUG HAVE BEEN MODIFIED SO AS TO                 00024650
C INCLUDE AN AVERAGING OVER THE INPUT SPECTRA                         00024660
C                                              RTI - WFH 1/13/79       00024670
          DO 50 I=1,13                                                 00024680
C INITIALIZE MAIN SPECTRUM ARRAY IN CORE FOR ADDITION                 00024690
          DO 31 IK=1,411                                               00024700
       31 SPEC(I,IK)=0                                                 00024710
C READ IN NAVG SPECTRA FOR THE CURRENT CORE POSITION                  00024720
          DO 40 IJ=1,NAVG                                              00024730
          IQUPD=0                                                      00024740
C IQUPD ENSURES THAT THE QUE IN THE I/O ROUTINES IS                   00024750
C UPDATED ONLY ONCE                                                   00024760
C 114 TELLS WHICH QUEUE LOCATION TO UPDATE                            00024770
          IF(IJ.EQ.NAVG)IQUPD=1                                       00024780
          CALL RDSPC(ISCNO,AVGSPC,I,IQUPD,EOF)                         00024790
          IQUPD=0                                                      00024800
          IF(EOF.EQ.0)GO TO 34                                         00024810
C EOF HAS BEEN ENCOUNTERED BEFORE ALL 13 CORE POSTIONS WERE FILLED    00024820
          WRITE(IPTR1,60)                                              00024830
       60 FORMAT('-','*** UNABLE TO FILL 13 CORE POSITIONS - EOF ***') 00024840
          STOP                                                         00024850
       34 CONTINUE                                                     00024860
C NOW INCREMENT MAIN ARRAY IN CORE                                    00024870
          DO 32 IK=1,411                                               00024880
       32 SPEC(I,IK)=SPEC(I,IK)+AVGSPC(IK)                             00024890
       40 CONTINUE                                                     00024900
C NOW DIVIDE BY NAVG IF NECESSARY                                     00024910
          IF(NAVG.EQ.1)GO TO 47                                        00024920
          DO 46 IK=1,411                                               00024930
       46 SPEC(I,IK)=SPEC(I,IK)/NAVG                                   00024940
       47 CONTINUE                                                     00024950
       50 CONTINUE                                                     00024960
C NOW SET INTERNAL SPECTRUM NUMBER                                    00024970
          SPCNO=ISCNO-6*NAVG-NAVG                                      00024980
          RETURN                                                       00024990
          END                                                          00025000
          SUBROUTINE SETGHY(NS,M,GNU,HNU,GPOS,HPOS,ISW,GMX)            00025010
C                                                                      00025020
C     *** THIS ROUTINE ACTUALLY DOES THE SETUP AND                     00025030
C     *** INTERPOLATION PRIOR TO DOUBLET RESOLUTION                    00025040
C ;   *** IT CALLS THE DOUBLET RESOLVER.                               00025050
C                                                                      00025060
          INTEGER NAME,RDATE,BITMAP,GCTIME,LIBMAP,INTEG,LOMASS         00025070
          INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO       00025080
 ;        INTEGER SPEC,IND,IR,BK,NM,NTM                                00025090
          INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7             00025100
          REAL    SPARE5,SPARE6                                        00025110
          INTEGER GPOS,HPOS    .                                       00025120
          INTEGER NUSPEC,NMASS,OVLAP,ISW                               00025130
          INTEGER STORE                                                00025140
          REAL    ISVP8,ISVP9                                          00025150
          REAL    DMX                                                  00025160
          REAL    GMX                                                  00025170
C                                                                      00025180
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      DIMENSION GNU(18),HNU(18),Y(18)                            00025190
      COMMON PKHIST(20),NPHIST(20)                               00025200
      COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5          00025210
      COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                  00025220
      COMMON SG,SG2,SIG,S1,S12,AN,AA,BB,CC,DD                    00025230
      COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                 00025240
      COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT        00025250
      COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                        00025260
      COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS           00025270
      COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)        00025280
      COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7    00025290
      COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                   00025300
      COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX        00025310
      COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5) 00025320
      COMMON /MODES/SGMODE(3),SHMODE(3),GMODE,HMODE              00025330
      COMMON /CRATMX/RATMXX                                      00025340
      INTEGER BEDROK                                             00025350
      DATA BEDROK/40/                                            00025360
C                                                                00025370
C                                                                00025380
C     DO ROTARY BUFFER INDEXING OF SPEC(14,NUMMASSES)            00025390
      J = 13                                                     00025400
      DO 1000 I=1,13                                             00025410
      K = J - 1                                                  00025420
      IJ = NS - K - 14 * ((NS - J)/14)                           00025430
      Y(I) = SPEC(IJ,M)                                          00025440
      J = J - 1                                                  00025450
1000  CONTINUE                                                   00025460
C     DO NOT LET ANY PEAKS WITH SATURATED VALUES IN THEIR        00025470
C     PROFILES PASS THROUGH DOUBLET RESOLVER.                    00025480
      DO 50 I= 1,11                                              00025490
      IF ( Y(I) .GE. SATVAL ) GO TO 5                            00025500
50    CONTINUE                                                   00025510
C                                                                00025520
C     WE TRY TO ELIMINATE BACKGROUND PEAKS FROM PASSING THROUGH  00025530
C     DOUBLET FILTER: SO, LET K1 = .0125 * Y(7), AND K2 = .0125 * G(7). 00025540
C     THEN: WHERE M = MAX*K1,K20. LET D = MIN*M,700.AND D = MAX*D,300   00025550
C              (WE USE AN ABSOLUTE MAX OF 70 SO AS NOT TO MISS HIGH MASS 00025560
C               PEAKS WITH SMALL CONTRIBUTIONS WHEN THE BASE PEAK IS     00025570
C               LARGE,AND A MIN OF 30 FOR LOW AMPLITUDE DRIBBLE.)        00025580
C                                                                00025590
C     ----------------------------------------------- <- Y(7) + E 00025600
C          .            .   .      .            E              00025610
C       .      .    * <- Y(7)         .       -               00025620
C      .    .        .                   E                    00025630
C     ----------------------------------------------- <- Y(7) - E 00025640
C                                                                00025650
C     IF THE FRAGMENTOGRAM STAYS IN THE ABOVE ENVELOPE FROM Y(3) TO 00025660
C     TO Y(11), THEN WE CONSIDER IT A BACKGROUND PEAK.           00025670
C                                                                00025680
C                                                                00025690
      D = .0125                                                  00025700
      K1 = D * Y(7)                                              00025710
C     WE MUST RECALL THAT G(7) HAS BEEN NORMALIZED IN GETHGT     00025720
      K2 = D * GNU(7)/GMX                                        00025730
      DMX = K1                                                   00025740
      IF ( DMX .LT . K2 ) DMX = K2                               00025750
C     DMX IS MAX*K1,K20                                          00025760
      IF( DMX .GT. 70) DMX = 70
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C          DMX = MIN*DMX,700                                  00025770
           IF(DMX .LT. BEDROK ) DMX   = BEDROK                00025780
C          DMX = MAX*BEDROK,DMX@                              00025790
           E1 = Y(7) + DMX                                    00025800
           E2 = Y(7) - DMX                                    00025810
           DO 100 I = 3,11                                    00025820
           IF (Y(I) .GT. E1   ,OR.   Y(I) .LT. E2) GO TO 200  00025830
100        CONTINUE                                           00025840
           GHGT = 0                                           00025850
           RETURN                                             00025860
200        CONTINUE                                           00025870
C                                                             00025880
C          WE NOW TRY TO ELIMINATE LOCALLY "NEARLY LINEAR"    00025890
C          CONTRIBUTIONS BY FITTING A LINE TO THE LOCAL FRAGMENTOGRAM  00025900
C          IN A LEAST SQUARES WAY, AND EXAMINING              00025910
C                                                             00025920
C             RATIO =   (ROOT MEAN SQUARE ERROR)/(AVERAGE VALUE OF Y(I))  00025930
C                                                             00025940
C                                                             00025950
C          THIS TEST HAS  BEEN VERY SUCESSFUL IN ELIMINATING COLUMN  00025960
C          BLEED .                                            00025970
           CALL BLEED(Y(5),RATIO)                             00025980
C THIS MOD INSERTED ON A TEMPORARY BASIS TO GATHER STATISTICS 00025990
C ON ERROR RATIO - CODE 3                                     00026000
C                            WFH RTI 9/31/78                  00026010
C          ITYP=3                                             00026020
C          ISPC=SPCNO    '                                    00026030
C          WRITE(20,6250) ITYP,ISPC,RATIO,RATIO               00026040
C6250 FORMAT(2A4,20X,2A4)                                     00026050
           IF (RATIO .GT. RATMXX) GO TO 290                   00026060
           GHGT = 0                                           00026070
           RETURN                                             00026080
290        CONTINUE                                           00026090
C      ALSO, IF Y(I) IS NON INCREASING FOR I=4,9, IE,Y(I) .GE. Y(I+1),  00026100
C          THEN DON'T CONSIDER, AS IT IS EITHER BACKGROUND    00026110
C          OR TAIL OF PRECEDING PEAK                          00026120
           DO 300 I = 4,9                                     00026130
           IF ( Y(I) .LT. Y(I+1) ) GO TO 400                  00026140
300        CONTINUE                                           00026150
           GHGT = 0                                           00026160
           RETURN                                             00026170
400        CONTINUE                                           00026180
           MI=M+39                                            00026190
C ARITHMETIC BELOW HAS BEEN REPLACED BY FUNCTION SUBROUTINE   00026200
C IN ORDER TO ACCOMODATE MAGNETIC INSTRUMENTS....             00026210
C                            RTI WFH 11/20/78                 00026220
C          TSHIFT = FLOAT(MI - LOMASS)/(HIMASS - LOMASS)      00026230
           TSHIFT = SCAN(MI)                                  00026240
C          INTERPOLATE PEAK PROFILE TO TIME COORDINATE OF MODEL PEAK,G  00026250
           CALL TIMESF(TSHIFT,Y(2),11,GMODE)                  00026260
C          CANNOT USE ENDPOINTS AFTER INTERPOLATION           00026270
C                                                             00026280
C                                                             00026290
C          *** NOW USE LEAST SQUARES DOUBLET RESOLVER TO GET       .    00026300
C          *** THE AMPLITUDE OF THE COMPONENT AT THE DETECTED SPECTRUM.  00026310
C                                                             00026320
C                                                             00026330
           IHSPEC = 6+(HPOS-1)/3                              00026340
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C          IHSPEC = 6 - 11                                        00026350
           STORE = 0                                              00026360
C          STORE WILL BE SET 1 BY DUBLET IF M QUALIFIES FOR NEW AMPLITUDE. 00026370
           CALL DUBLET(GNU,HNU,Y,STORE,M,IHSPEC,GHGT,ISW,NS)      00026380
C                                                                 00026390
C          SAVE THE COMPONENT CONTRIBUTING TO  THE DETECTED SPECTRUM. 00026400
C                                                                 00026410
C                                                                 00026420
C          SAVE CONTRIBUTION WITH MINIMUM ERROR.                  00026430
C                                                                 00026440
           IF (GHGT .GT. 32767) GHGT = 32767                      00026450
C          MADE SURE NO INTEGER OVERFLOW                          00026460
           IF (GHGT .LE. 10) GHGT = 0                             00026470
C          HEIGHTS LE 10 ARE CONSIDERED ARTIFACTS OF THE DOUBLET RESOLVER 00026480
           IF(STORE .EQ. 1) NUSPEC(M)=GHGT                        00026490
C                                                                 00026500
5          RETURN                                                 00026510
           END                                                    00026520
C          THIS SUBROUTINE DOES ALL PRINTING                      00026530
C          FOR CLEANUP. PLEASE USE IT TO ADD NEW PRINTING         00026540
C          IN ANY SUBROUTINE.                                     00026550
C          THE CALL STATEMENT ALLOWS FOR PASSING OF ARRAYS        00026560
C          REALS AND INTEGERS.                                    00026570
C          THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT 00026580
C          FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND 00026590
C          GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00026600
C          (GRANT NGR-05-020-632).                                00026610
           SUBROUTINE SPEPRT(N,IAR,AR,R1,R2,R3)                   00026620
           INTEGER N,IONE,NINE,MAD                                00026630
           REAL R1,R2,R3                                          00026640
C THE DIMMENSIONS OF AR AND IAR HAVE BEEN SET TO (1),(1) FROM     00026650
C TO HELP WITH WATFIV....                                         00026660
C                                          WFH RTI 4/30/78        00026670
           DIMENSION IAR(1),AR(1)                                 00026680
           COMMON /DUBBUG/IFLAG                                   00026690
           COMMON /IMAD/MAD                                       00026700
           COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT         00026710
           DATA IONE,NINE/1,9/                                    00026720
C          IFLAG IS RESET IF NO PRINTING IS TO BE DONE/           00026730
           IF (IFLAG.EQ.0) RETURN                                 00026740
           GO TO (40,50,60,70),N                                  00026750
C          THE ABOVE IS A CASE STATEMENT FOR EXECUTING PRINT      00026760
C          OPTIONS.C                                              00026770
C          NOW DO STALSO OUTPUT                                   00026780
40         IIAR=IAR(1)-MAD                                        00026790
           WRITE(IPTR2,600) IIAR                                  00026800
           RETURN                                                 00026810
C          THE ABOVE WRITE IS FOR MASS OF SATURATION              00026820
50         WRITE(IPTR2,550) R1                                    00026830
           WRITE(IPTR2,610)                                       00026840
           IUP = IAR(1)                                           00026850
           WRITE(IPTR2,535) (AR(I),I=IONE,IUP)                    00026860
           RETURN                                                 00026870
60         WRITE(IPTR2,800)                                       00026880
           WRITE(IPTR2,560) AR(1),R1,R2,R3                        00026890
           WRITE(IPTR2,900)                                       00026900
C          WRITES RPKHGT,LOCAL BACKGROUND,RATIO,G(5)              00026910
           RETURN                                                 00026920
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70      WRITE(IPTR2,700)
C       THE ABOVE WRITES SATURATED DEFAULT VALUE.                        00026930
        RETURN                                                           00026940
C       FORMAT STATEMENTS FOLLOW.                                        00026950
535     FORMAT(/,8X,7F7.0,/,8X,6F7.0,/)                                  00026960
550     FORMAT(8X,/'    SATURATED VALUE = ',F7.1)                        00026970
560     FORMAT(8X,' PEAK HEIGHT =',F7.0,/,8X,' BACK GROUND =',F7.0,      00026980
       -/,8X,' PEAK TO MODLEL RATIOS AVERAGE, RATIO =',E15.8,/,8X,       00026990
       -/,' G(5) =',F7.0,//)                                            00027000
600     FORMAT(/,' SATURATION ENCOUNTERED, MASS = ',I4,/)               00027010
610     FORMAT(' SATURATED PEAK PROFILE FOLLOWS ',/)                     00027020
700     FORMAT(/,' SUPER SATURATION ENCOUNTERED ',/,8X,                  00027030
       -'PEAK HEIGHT DEFAULTS TO MAXIMUM VALUE '//)                      00027040
800     FORMAT(/' SATURATED PEAK ANAYLSIS  '/)                           00027050
  900 FORMAT(/' NOTE: PEAK HEIGHT = RATIO X G(5)'/)                      00027060
        END                                                              00027070
        SUBROUTINE TIMESF(DELTIM,Y,N,GTIME)                              00027080
        REAL    GTIME                                                    00027090
        INTEGER N                                                        00027100
        REAL    RATE,DELTIM                                              00027110
C Y HAS BEEN REDIMENSIONED DOWN FROM 15 TO 1                             00027120
C TO MAKE THIS THING WATFIV COMPATABLE  -  WFH RTI 4/25/78              00027130
        DIMENSION   Y(1)                                                 00027140
C                                                                        00027150
C                                                                        00027160
C       THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT     00027170
C       FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND        00027180
C       GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  00027190
C       (GRANT NGR-05-020-632).                                          00027200
C                                                                        00027210
C       THIS SUBROUTINE TIME ALIGNS A PEAK AT A GIVEN MASS   M  TO       00027220
C       THE SAME TIME CO-ORDINATE SYSTEM AS THE MODEL'S  MASS.           00027230
C       (THE TIME CO-ORDINATE  IS  GTIME FOR MODEL)                      00027240
C                                                                        00027250
C           DELTIM=(M-LOMASS)/(HIMASS-LOMASS)                            00027260
C                                                                        00027270
C           Y IS THE ABCISSAS OF THE FRAGMENTOGRAM AT MASS M.         '  00027280
C                                                                        00027290
C       THIS ALIGNMENT IS DONE BY A CUBIC FIT USING  LAGRANGE'S          00027300
C       METHOD.I.E., GIVEN THE 4 POINTS  X0,X1,X2,X3, WE FIND L(X) AS    00027310
C       FOLLOWS:                                                         00027320
C                                                                        00027330
C           L(X)=^(X-X1)(X-X2)(X-X3)/((X0-X1)(X0-X2)(X0-X3))@Y0 +        00027340
C                ^(X-X0)(X-X2)(X-X3)/((X1-X0)(X1-X2)(X1-X3))@Y1 +        00027350
C                ^(X-X0)(X-X1)(X-X3)/((X2-X0)(X2-X1)(X2-X3))@Y2 +        00027360
C                ^(X-X0)(X-X1)(X-X2)/((X3-X0)(X3-X1)(X3-X2))@Y3          00027370
C                                                                        00027380
C           WITH THE X'S INTEGRALLY SPACED.                             00027390
C                                                                        00027400
C       IN EACH CASE WE INTERPOLATE FOR A NEW MIDDLE POINT,OR           00027410
C       L(X1+DX). SO, THE ABOVE EQUATION REDUCES TO                      00027420
C                                                                        00027430
C           L(X1+DX) = C0 * Y0 + C1 * Y1 + C2 * Y2 + C3 * Y3             00027440
C                                                                        00027450
C       C0 = DX * (DX-1)(DX-2)/-6                                        00027460
C   C1 = (DX+1)(DX-1)(DX-2)/2                                            00027470
C   C2 = (DX+1)(DX)(DX-2)/-2                                             00027480
C   C3 = (DX+1)(DX)(DX-1)/6                                              00027490
C                                                                        00027500
```

```fortran
C         WHERE DX = GTIME  -  DELTIM
C
      INTEGER I
      REAL     C1,C2,C3,DTIME
      REAL     Y1,Y11,YMID,K1,K2,K3,K4,DXPOS
      DIMENSION YOLD(15)
C
C
C
      DO 50 I=1,N
      YOLD(I) = Y(I)
50    CONTINUE
C
C         SAVED OLDIES
C
      DX = GTIME - DELTIM
      DXPOS = DX
      IF ( DXPOS .LT. 0 ) DXPOS = -DX
      IF ( DXPOS .LT. 0.00001) RETURN
C       DON'T INTERPOLATE FOR SMALL VALUES OF DX
      K1 = DX - 1
      K2 = DX - 2
      K3 = DX + 1
      K4 = DX + 2
      C1= (DX * (K1) * (K2))/(-6)
      C2= ((K3) * (K1) * (K2))/2
      C3= ((K3) * (DX) * (K2))/(-2)
      C4= ((K3) * (DX) * (K1))/6
C
C         INTERPOLATE
C
      JN = N - 2
      DO 100 I=2,JN
      Y(I)=C1*YOLD(I-1) + C2*YOLD(I) + C3*YOLD(I+1) + C4 * YOLD(I+2)
100   CONTINUE
      E1= C4
      E2= ((K4) * (DX) * (K1))/2
      E3= ((K4) * (K3) * (K1))/(-2)
      E4= ((K4) * (K3) * (DX))/6
      NN = N - 1
      Y(NN) = Y(N-3) * E1 + Y(N-2) * E2 + Y(NN) * E3 + Y(N) * E4
C
      DO 275 I = 2,NN
      IF(Y(I) .LT. 0) Y(I) = 0
275   CONTINUE
      RETURN
      END
      SUBROUTINE TLOC(NS,M1,M2,M3,IFOUND,EOF)
C       THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT
C       FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND
C       GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
C       (GRANT NGR-05-020-632).
C       *** THE MAIN FUNCTION OF THIS ROUTINE IS TO EXAMINE
C       *** THE CURRENT DATA IN THE PROCESSING WINDOW
C       *** AND DETECT WHEN THERE IS A COMPONENT PRESENT IN THE
C       *** WINDOW. THIS IS DONE BY KEEPING A HISTOGRAM OF
C       *** HOW MANY PEAK MODES ARE MAXIMIZING WITHIN
C       *** THE WINDOW. A HISTOGRAM IS ALSO KEPT OF THE
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C       *** ION CURRENTS ASSOCIATED WITH THE PEAKS THAT ARE        00028090
C       *** ARE MAXIMIZING. THIS LATTER MEASURE IS MORE            00028100
C       *** EFFECTIVE FOR COMPONENT DETECTION. AN INDEX            00028110
C       *** SET IS KEPT OF THOSE MASSES THAT HAVE MAXIMIZED        00028120
C       *** IN THE WINDOW (ARRAY 'IND'). DURING THIS WHOLE         00028130
C       *** PROCESS A MODEL PEAK FOR THE COMPONENT IS ALSO         00028140
C       *** CHOSEN 'GPEAK' USING A SHARPNESS CRITERION.            00028150
C PARAMETER EOF ADDED - SEE COMMENT NEAR CALL STMT IN MAIN         00028160
C                                           WFH RTI 9/31/78        00028170
        INTEGER NAME,RDATE,BJTMAP,GCTIME,LIBMAP,INTEG,LOMASS       00028180
        INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO     00028190
        INTEGER SPEC,IND,IR,BK,NM,NTM,RECNO,FLAG,KSTOR(50),MAD,    00028200
       1KMAD(2,50)                                                 00028210
        INTEGER NUSPEC,NMASS,OVLAP,EOF                             00028220
        INTEGER MODBKG,LOCLBG                                      00028230
        INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7           00028240
        INTEGER  FSTREC,AJACEN,AHEAD                               00028250
        REAL    SPARE5,SPARE6                                      00028260
C THIS HAS BEEN INSERTED FOR THE AVERAGING FACILITY                00028270
C                                       RTI WFH 1/14/79            00028280
        INTEGER NAVG,HAVG,AVGSPC(411)                              00028290
        REAL*8 TLC/' TLOCXX '/                                     00028300
        REAL    ISVP8,ISVP9                                        00028310
C THE IDENTIFIER DIB HAS BEEN CHANGED TO SCAN TO MAKE              00028320
C WAY FOR THE NEWLY INCORPORATED FUNCTION SUBROUTINE               00028330
C                                       WFH RTI 9/31/78            00028340
        REAL    F1,F2,F3,YTOP,HIST(7),SLOPE,SCAN                   00028350
        COMMON PKHIST(20),NPHIST(20)                               00028360
        COMMON YM5(11)                                             00028370
        COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                  00028380
        COMMON SG,SG2,SIG,SI,SI2,AN,AA,BB,CC,DD                    00028390
        COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                 00028400
        COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT        00028410
        COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                        00028420
        COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS           00028430
        COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)        00028440
        COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7    00028450
        COMMON RATMIN,RATEMX,SIGYB,SIGNXT,SIGLST                   00028460
        COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX        00028470
        COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5) 00028480
        COMMON /DUBBUG/IDEBUG                                      00028490
        COMMON /MODES/SGMODE(3),SHMODE(3),GMODE,HMODE              00028500
        COMMON /MASSES/ISGMAS(3),ISHMAS(3),IGMASS,IHMASS           00028510
        COMMON /IFF/IFLAG(3)                                       00028520
        COMMON /AJACNT/AJACEN(2)                                   00028530
        COMMON /PARAMS/MINTIC,MINNY,NTHIRD,RATM                    00028540
        COMMON /LFTRIT/ILEFT,IRIGHT                                00028550
        COMMON /HIND/IH1,IH2,MSINGS(2,50),MINX,LINGS(50),LINX      00028560
C       COMMON /CRAWBU/RAWBUF(411)                                 00028570
        COMMON /CFSTRE/FSTREC                                      00028580
        COMMON /AVG/ NAVG,HAVG                                     00028590
        COMMON /CAHEA/AHEAD(5)                                     00028600
        COMMON /IMAD/MAD                                           00028610
C       MSINGS SAVES MASSES  OF SINGLETS IN  HISTOGRAMS.           00028620
        EQUIVALENCE (YM4,YM5(2))                                   00028630
        EQUIVALENCE (YM3,YM5(3)),(YM2,YM5(4)),(YM1,YM5(5))         00028640
        EQUIVALENCE (Y0,YM5(6)),(YP1,YM5(7)),(YP2,YM5(8))          00028650
        EQUIVALENCE (YP3,YM5(9)),(YP4,YM5(10)),(YP5,YM5(11))       00028660
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      DATA HIST/-.3333.0...3333..6667.1.0.1.3333.1.6667/        00028670
C     *** CIRCULAR QUEUE TO CONTROL CURRENT DATA SET             00028680
      I1=NS-13-14*((NS-14)/14)                                   00028690
      I2=NS-12-14*((NS-13)/14)                                   00028700
      I3=NS-11-14*((NS-12)/14)                                   00028710
      I4=NS-10-14*((NS-11)/14)                                   00028720
      I5=NS-9-14*((NS-10)/14)                                    00028730
      I6=NS-8-14*((NS-9)/14)                                     00028740
      I7=NS-7-14*((NS-8)/14)                                     00028750
      I8=NS-6-14*((NS-7)/14)                                     00028760
      I9=NS-5-14*((NS-6)/14)                                     00028770
      I10=NS-4-14*((NS-5)/14)                                    00028780
      I11=NS-3-14*((NS-4)/14)                                    00028790
      I12=NS-2-14*((NS-3)/14)                                    00028800
      I13=NS-1-14*((NS-2)/14)                                    00028810
      I14=NS-14*((NS-1)/14)                                      00028820
C     *** READ IN NEXT SPECTRUM                                  00028830
C     NOTE: NS = 14.15.....MAXSPEC - 10                          00028840
C           FIRST RECORD TO BE READ IS NUMBER 13.                00028850
      RECNO = NS                                                 00028860
      INSLT=1                                                    00028870
C                                                                00028880
C THE PRIMARY INPUT STATEMENT HAS BEEN MODIFIED TO INCLUDE       00028890
C AN AVERAGING FACILITY OVER NAVG INPUT SPECTRA                  00028900
C                                RTI - WFH 1/13/79               00028910
C INITIALIZE CURRENT SPECTRUM IN CORE                            00028920
      DO 90 IK=1.411                                             00028930
   90 SPEC(I14.IK)=0                                             00028940
C ADD AS MANY INPUT SPECTRA AS NECESSARY TO CORE SPECTRUM        00028950
      DO 92 IJ=1.NAVG                                            00028960
C IOUPD ENSURES THAT THE QUEUE DOWN INSIDE THE READ ROUTINES IS  00028970
C UPDATED ONLY ONCE OVER THE SPREAD OF NAVG INPUT SPECTRA        00028980
      IOUPD=0                                                    00028990
      IF(IJ.EQ.HAVG)IOUPD=1                                      00029000
C IOUPD TELLS WETHER OR NOT TO UPDATE READ ROUTINE QUEUE         00029010
C I14 TELLS RDSPC QUEUE POSITION                                 00029020
      CALL RDSPC(ISCNO.AVGSPC.I14.IOUPD.EOF)                     00029030
      IOUPD=0                                                    00029040
      IF(EOF.EQ.0)GO TO 4                                        00029050
      RETURN                                                     00029070
C READ ONWARD...                                                 00029080
    4 CONTINUE                                                   00029090
      DO 97 IK=1.411                                             00029100
   97 SPEC(I14.IK)=SPEC(I14.IK)+AVGSPC(IK)                       00029110
   92 CONTINUE                                                   00029120
C DIVIDE AS NECESSARY                                            00029130
      IF(NAVG.EQ.1)GO TO 94                                      00029140
      DO 95 IK=1.411                                             00029150
   95 SPEC(I14.IK)=SPEC(I14.IK)/NAVG                             00029160
   94 CONTINUE                                                   00029170
C NOW UPDATE SPECTRUM NUMBER                                     00029180
      SPCNO=ISCNO-7*NAVG+HAVG-1                                  00029190
C THE FOLLOWING TEN STMENTS OR SO HAVE BEEN DISCARDED            00029200
C TO MAKE WAY FOR MULTIPLE RUN PROCESSING AS WELL                00029210
C AS THE COMMON BLOCK /CRAWBU/ AS NEITHER SERVES ANY             00029220
C USEFULL PURPOSE.                                               00029230
C                         WFH - RTI                              00029240
C                         12/6/78                                00029250
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C        GO TO 620                                               00029260
C2       WRITE(IPTR2,31)                                         00029270
C    2 CALL TLPRNT(3,NPHIST,PKHIST,XY,XY,XY,1,1,1)               00029280
C        STOP 16                                                 00029290
C   31 FORMAT(' ***FATAL READ ERROR ON MAIN INPUT FILE-IN TLOC***') 00029300
C        RETURN                                                  00029310
C620     DO 10 M=1,NMASS                                         00029320
C10      SPEC(114,M) = RAWBUF(M)                                 00029330
C        NOW, WE'RE OFF AND RUNNING WHILE THE DISK IS HUMMING ....  00029340
         NS3=NS-11                                               00029350
         M3=NS3-3*((NS3-1)/3)                                    00029360
         M2=NS3-1-3*((NS3-2)/3)                                  00029370
         M1=NS3-2-3*((NS3-3)/3)                                  00029380
         RMAX(M3)=0.0                                            00029390
         SGMODE(M3)=0                                            00029400
         BK(M3)=0                                                00029410
         IR(M3)=0                                                00029420
         ISGMAS(M3) = -1                                         00029430
         NMAX=0                                                  00029440
         SIGMA7=0.0                                              00029450
         IFLAG(M3) = 0                                           00029460
         NAVE = 0                                                00029470
C        LINGS IS SET UP IN NXTMAX AND CONTAINS STUFF FROM HIST 10,11 00029480
C        WHICH BECOMES HIST OF 7,8 HERE.                         00029490
         DO 12 I = 1,50                                          00029500
         MSINGS(IH1,I) = MSINGS(IH2,I)                           00029510
12       MSINGS(IH2,I) = LINGS(I)                                00029520
C        SET MINX FOR STORING IN MSINGS.                         00029530
         DO 13 I = 1,49                                          00029540
         IF (LINGS(I) .EQ. 0) GO TO 14                           00029550
13       CONTINUE                                                00029560
14       MINX = I                                                00029570
         LINX = I                                                00029580
         DO 17 J = 1,I                                           00029590
17       LINGS(J) = 0                                            00029600
         NINX = I                                                00029610
         DO 18 I = 1,50                                          00029620
         IF(MSINGS(IH1,I) .EQ. 0 ) GO TO 19                      00029630
18       CONTINUE                                                00029640
19       CONTINUE                                                00029650
         NINX = I                                                00029660
C        OINX IS USED FOR STORING HISTOGRAMED MASSES IN H(5-6)   00029670
C        NOW MOVE DETECTION FLAG FOR PREVIOUS SPECTRUM INTO      00029680
C        THE FLAG FOR ITS IMMEDIATE PREDECESSOR.THIS IS USED     00029690
C        IN GETHGT SO SINGLETS FROM IMMEDIATED PREDECESSORS      00029700
C        ARE NOT INCLUDED IN THEIR IMMEDIATE SUCESSORS.          00029710
         AJACEN(1) = AJACEN(2)                                   00029720
         AJACEN(2) = 0                                           00029730
C        LOOP THROUGH ALL MASSES      AND RESET FOUND INDICES.   00029740
         DO 15 M=1,411                                           00029750
15       IND(M3,M)=0                                             00029760
         NPHIST(8)= ISVN8    .                                   00029770
         NPHIST(9)= ISVN9                                        00029780
         PKHIST(8)= ISVP8                                        00029790
         PKHIST(9)= ISVP9                                        00029800
         DO 16 J=1,6                          .                  00029810
         PKHIST(J)=PKHIST(J+3)                                   00029820
16       CONTINUE                                                00029830
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C         PKHIST(1)+PKHIST(4),....,PSHIST(6)+PKHIST(9)           00029840
          PKHIST(7)= (SPARE5)                                    00029850
          PKHIST(8)= (SPARE6)                                    00029860
          PKHIST(9)=0                                            00029870
          DO 231 J=1,6                                           00029880
          NPHIST(J)=NPHIST(J+3)                                  00029890
231       CONTINUE                                              00029900
C         NPHIST(1)+NPHIST(4),....,NPHIST(6)+NPHIST(9)          00029910
          NPHIST(7)= SPARE3                                      00029920
          NPHIST(8)= SPARE4                                      00029930
          NPHIST(9)=0                                            00029940
          NPHIST(10)=0                                           00029950
          NPHIST(11)=0                                           00029960
          PKHIST(10)=0                                           00029970
          PKHIST(11)=0                                           00029980
          DO 43 I = 2,5                                          00029990
43        AHEAD(I-1) = AHEAD(I)                                  00030000
          AHEAD(5) = 0                                           00030010
C         THE ABOVE IS A BINARY LIST OF SPECTRA DETECTED AHEAD.  00030020
C         WE SHIFT IT LEFT AT EACH NEW SPECTRUM SEARCH.IT IS     00030030
C         USED TO GUARANTEE ANY SPECTRUM DETECTED AHEAD IS ALWAYS 00030040
C         PROCESSED.                                             00030050
C STATEMENT REMOVED BECAUSE NO LONGER NEEDED WITH SCAN ROUTINE   00030060
C                                           WFH RTI 9/31/78      00030070
C         DIB = HIMASS - LOMASS                                  00030080
          DO 70 M=1,411                                          00030090
C         RUN THROUGH MASSES                                     00030100
          Y0=SPEC(I8,M)                                          00030110
C         SAVE FOR CLEAN UP RATIO, TICRAT                        00030120
          SIGMA7 = SIGMA7 + Y0                                   00030130
          IF(Y0.GE.SATVAL) GO TO 65                              00030140
C         *** MARK SATURATED MASSES FOR LATER PROCESSING         00030150
          YM1=SPEC(I7,M)                                         00030160
          YP1=SPEC(I9,M)                                         00030170
C         TEST FOR SINGLET                                       00030180
C                                                                00030190
C            .    .                                             00030200
C         .    Y0         .           .        <-- SHAPE REQUIREMENT. 00030210
C                                                                00030220
C    .                            .                              00030230
C  .                   YP4                                       00030240
          IF(Y0 .LE. YM1) GO TO 70                               00030250
          IF(Y0 . LE. YP1) GO TO 70                              00030260
          YM2=SPEC(I6,M)                                         00030270
          YP2=SPEC(I10,M)                                        00030280
          YM3=SPEC(I5,M)                                         00030290
          YP3=SPEC(I11,M)                                        00030300
          YM4 =SPEC(I4,M)                                        00030310
          YP4=SPEC(I12,M)                                        00030320
          YM5(1)=SPEC(I3,M)                                      00030330
          YP5=SPEC(IJ3,M)                                        00030340
          YY5=YM5(1)                                             00030350
C         TEST LEFT SLOPE OF PEAK                                00030360
C         ILEFT IS REQUIRED NUMBER OF STRICKLY DECREASING LEFT POINTS 00030370
          IF(YM1 .LE. YM2) GO TO 65                              00030380
          IF(ILEFT .EQ. 2) GO TO 44                              00030390
          IF(YM2 .LE. YM3) GO TO 65                              00030400
          IF(ILEFT .EQ. 3) GO TO 44                              00030410
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          IF(YM3 .LE. YM4) GO TO 65                                    00030420
44        CONTINUE                                                     00030430
C         TEST RIGHT SLOPE OF PEAK                                     00030440
C         IRIGHT IS REQUIRED NUMBER OF STRICKLY DECREASING RIGHT POINTS 00030450
          IF(YP1 .LE. YP2) GO TO 65                                    00030460
          IF(IRIGHT .EQ. 2) GO TO 45                                   00030470
          IF(YP2 .LE. YP3) GO TO 65                                    00030480
          IF(IRIGHT .EQ. 3) GO TO 45                                   00030490
          IF(YP3 .LE. YP4) GO TO 65                                    00030500
45        CONTINUE                                                     00030510
C         CALCULATE VALUE AT MODE OF PEAK,YTOP, AND                    00030520
C         X DISPLACEMENT,XTOP.                                         00030530
          CALL NEWTOP(YM5,RATE,XTOP,YTOP,4)                            00030540
C         IF XTOP IS OUT OF RANGE THE PEAK IS NOT ELUTING HERE OR      00030550
C         THE DATA HAS TOO MANY INFLECTION POINTS                      00030560
          IF(XTOP .LE. -1.  .OR.  XTOP .GE. 1.) GO TO 65               00030570
C         MAKE SURE THE PEAK IS INCREASING FASTER THAN BACKGROUND      00030580
          IF( (YTOP - YY5).LT.30  .AND.  (YTOP - YP5).LT.30 ) GOTO 70  00030590
C         SEE IF QUALIFIES FOR MODEL FROM RATE.                        00030600
          IF(YTOP.GE.SATVAL.OR.YP1.GE.SATVAL.OR.YM1.GE.SATVAL)GO TO 65 00030610
          IF(YP2.GE.SATVAL.OR.YP3.GE.SATVAL.OR.YP4.GE.SATVAL) GO TO 65 00030620
          IF(YM2.GE.SATVAL.OR.YM3.GE.SATVAL.OR.YM4.GE.SATVAL)GO TO 65  00030630
C         PREVENT SUPER SATURATION BY ABOVE                            00030640
C         SEE IF RATE IS MAXIMUM TO QUALIFY AS MODEL PEAK              00030650
          MODEL = 0                                                    00030660
          MI = M + 39                                                  00030670
          SLOPE = (YP5 - YY5)/10                                       00030680
          LOCLBG = YY5 + SLOPE * 5                                     00030690
C CHANGED TO HAVE FUNCTION SUBROUTINE TO HAVE DIFFERENT INSTRUMENTS    00030700
C                                      WFH RTI 9/31/78                  00030710
          TSHIFT=SCAN(MI)                                              00030720
C         TSHIFT = (MI - LOMASS)/DIB                                   00030730
          IF(RATE.LT.RMAX(M3)) GO TO 50                                00030740
          MODEL = 1                                                    00030750
          IF((YTOP - YY5) .GE. 160) GO TO 2000                         00030760
          IFLAG(M3) = 1                                                00030770
C         FLAG AS FUNNY MODEL                                          00030780
          GO TO 2500                                                   00030790
2000      IFLAG(M3) = 0                                                00030800
2500      CONTINUE                                                     00030810
          RMAX(M3)=RATE                                                00030820
          IR(M3)=M                                                     00030830
C         USE LINEAR BACKGROUND AS FIRST CUT APPROXIMATION             00030840
          MODBKG = SPEC(I1,M)                                          00030850
          IF ( MODBKG .GT. SPEC(I2,M) ) MODBKG = SPEC(I2,M)            00030860
          IF ( MODBKG .GT. SPEC(I3,M) ) MODBKG = SPEC(I3,M)            00030870
          IF ( MODBKG .GT. SPEC(I4,M) ) MODBKG = SPEC(I4,M)            00030880
          IF ( MODBKG .GT. SPEC(I5,M) ) MODBKG = SPEC(I5,M)            00030890
          IF ( MODBKG .GT. SPEC(I11,M) ) MODBKG = SPEC(I11,M)          00030900
          IF ( MODBKG .GT. SPEC(I12,M) ) MODBKG = SPEC(I12,M)          00030910
          IF ( MODBKG .GT. SPEC(I13,M) ) MODBKG = SPEC(I13,M)          00030920
          IF ( MODBKG .GT. SPEC(I14,M) ) MODBKG = SPEC(I14,M)          00030930
C         MODBKG = MIN * SPEC(IJ,M) : I1 .LE.  IJ  .LE. I140           00030940
          DO  40    IJ = 1,11                                          00030950
          GPEAK(M3,IJ) = YM5(IJ) - MODBKG                              00030960
40        CONTINUE                                                     00030970
          ISGMAS(M3) = MI                                              00030980
          SGMODE(M3)=TSHIFT                                            00030990
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          BK(M3) = MODBKG                                        00031000
50        CONTINUE                                               00031010
          XY=YTOP - (LOCLBG)                                     00031020
          IF ( XY .LE. 0 ) XY = 1.0                              00031030
C SIGY0 (EXCEPT IN COMMON DECLARATIONS) APPEARS ONLY IN THIS     00031040
C STATEMENT. HENCE IT HAS BEEN COMMENTED OUT.                    00031050
C                                WFH AT RTI        4/19/78        00031060
C         SIGY0=SIGY0 +  XY                                      00031070
          TITTY = TSHIFT + XTOP                                  00031080
          DO 800 IJ = 1,7                                        00031090
          IF (TITTY .LT. HIST(IJ)) GO TO 900                     00031100
800       CONTINUE                                               00031110
900       IH = 4 + IJ                                            00031120
C         IH = 5 TO 11                                           00031130
C         HISTOGRAM DATA PKHIST FOR INTENSITY. NPHIST FOR COUNT OF PEAKS  00031140
          PKHIST(IH)=PKHIST(IH) + XY                             00031150
          NPHIST(IH)=NPHIST(IH)+1                                00031160
C         SAVE MODE OF MODEL PEAK                                00031170
C         RESET MODEL FLAG                                       00031180
          IF ( MODEL .EQ. 1 ) GO TO 925                          00031190
C         ALWAYS LOG MASS OF MODEL.                              00031200
          NGOGO = IH - 4                                         00031210
C         NGOGO = 1,2,3,4,5,6,7                                  00031220
          GO TO ( 950,950,925,925,925,960,960 ), NGOGO           00031230
C  SLOT              5    6    7    8    9   10   11              00031240
C         HISTOGRAM SLOTS 7,8,9 0                                00031250
925       MSINGS(IH2,MINX) = MI                                  00031260
          MINX = MINX + 1                                        00031270
          IF(MINX .EQ. 51) MINX = 50                             00031280
          IF ( MODEL .EQ. 1 ) GO TO 950                          00031290
          GO TO 990                                              00031300
950       CONTINUE                                               00031310
C         HISTOGRAM SLOTS 5,6                                    00031320
          IF ( IH .GE. 7 ) GO TO 960                             00031330
          MSINGS(IH1,NINX) = MI                                  00031340
          NINX = NINX + 1                                        00031350
          IF(NINX .EQ. 51) NINX = 50                             00031360
          IF ( MODEL .EQ. 0 ) GO TO 990                          00031370
C             WE HAVE A POSSIBLE MODEL FOR PREVIOUS SPECTRUM SO  00031380
C             IF THE RATE CRITERIA IS SATISFIED. SAVE IT.        00031390
          IF ( RATE .LE. RMAX(M2) ) GO TO 990                    00031400
          ISGMAS(M2) = MI                                        00031410
          RMAX(M2) = RATE                                        00031420
          IFLAG(M2) = 0                                          00031430
          DO 970 IM = 1,11                                       00031440
970       GPEAK(M2,IM) = GPEAK(M3,IM)                            00031450
C         HISTOGRAM SLOTS 10,11                                  00031460
960       CONTINUE                                               00031470
          IF ( IH .LT. 10 ) GO TO 990                            00031480
          LINGS(LINX) = MI                                       00031490
          LINX = LINX + 1                                        00031500
          IF(LINX .EQ. 51) LINX = 50                             00031510
990       CONTINUE                                               00031520
C         SAVE MAXIMUM OF 50 MASSES DUE TO CORE LIMITATIONS      00031530
65        CONTINUE                                               00031540
          NMAX=NMAX+1                                            00031550
C         SAVE MASS THAT IS CONSIDERED A CONTRIBUTION            00031560
C         NMAX IS NUMBER OF MASSES MAXIMIZING .                  00031570
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      IND(M3,M) = M                                                00031580
70    CONTINUE                                                      00031590
C     NOW CHECK FOR DETECTED SPECTRUM IN ↑4,5,6@                    00031600
      NL=1                                                          00031610
      NU=9                                                          00031620
      IDXL=4                                                        00031630
      IDXU=6                                                        00031640
      SPARE3=NPHIST(10)                                             00031650
      SPARE4=NPHIST(11)                                             00031660
      SPARE5=PKHIST(10)                                             00031670
      SPARE6=PKHIST(11)                                             00031680
      ISVN8=NPHIST(8)                                               00031690
      ISVN9=NPHIST(9)                                               00031700
      ISVP8=PKHIST(8)                                               00031710
      ISVP9=PKHIST(9)                                               00031720
      CALL DETEKT(PKHIST,NPHIST,IFOUND,NLWCUT,NUPCUT                00031730
     &  ,NL,NU,IDXL,IDXU,MODE1)                                     00031740
C     MODE1 IS THE LOCATION HISTOGRAMICALLY OF THE SPECTRUM,        00031750
C     4.LTE.MODE1.LTE.6                                             00031760
C     IFOUND IS 1 IF SPECTRUM DETECTED.                            00031770
C PUT IN HEURISTIC FIX FOR THE CASE WHERE NO SUITABLE              00031780
C MODEL IS FOUND - INSERTED AT RTI BY WFH - 5/23/78                00031790
C                                                                  00031800
      IF(ISGMAS(M3).EQ.-1.AND.ISGMAS(M2).EQ.-1)IFOUND=0            00031810
      IF (IFOUND.NE.1) GO TO 888                                    00031820
      AJACEN(2) = 1                                                 00031830
C     SETS SPECTRUM DETECTED FLAG.                                 00031840
C TEMPORARY MOD HAS BEEN ADDED TO GATHER STATISTICS ON             00031850
C PEAK RATES-                RTI WFH 9/31/78                        00031860
C     IOBS=1                                                        00031870
C     WRITE(20,6251) IOBS,SPCNO,RMAX(M3)                           00031880
C6251 FORMAT(A4,A4,12X,A4)                                          00031890
      IF (RMAX(M3) .GE. RATM) GO TO 889                            00031900
      AJACEN(2) = 0                                                 00031910
      IFOUND = 0                                                    00031920
C..       CALL PUTNUM('SPEC. REJECTED FOR MIN. RATE, SPEC =',SPCNO) 00031930
C..       CALL PUTFLT('    RATE = ',RMAX(M3))                       00031940
      CALL TLPRNT(4,NPHIST,PKHIST,RMAX(M3),XY,XY,SPCNO,1,1)         00031950
C     WRITE(IPTR2,32)SPCNO,RMAX(M3)                                00031960
C32   FORMAT(' SPEC. REJECTED FOR MIN. RATE, SPEC = ',I6/' RATE = ',F1000031970
C    *.3/)                                                          00031980
      GO TO 888                                                     00031990
889   CONTINUE                                                      00032000
C     IFOUND = 1 IF SPECTRUM DETECTED.                             00032010
      CALL TLPRNT(1,SPEC,SPEC,XY,XY,XY,SPCNO,NLWCUT,NUPCUT)         00032020
      CALL TLPRNT(2,NPHIST,PKHIST,XY,XY,XY,1,1,1)                   00032030
      IF ( IDEBUG .EQ. 0 ) GO TO 888                               00032040
      CALL TLPRNT(5,NPHIST,PKHIST,XY,XY,XY,1,1,1)                   00032050
C     WRITE(IPTR2,5000)                                            00032060
      DO 9 KX=1,2                                                   00032070
      DO 9 KZ=1,50                                                  00032080
      KMAD(KX,KZ)=MSINGS(KX,KZ)-MAD                                 00032090
      IF(KMAD(KX,KZ).LE.0)KMAD(KX,KZ)=0                             00032100
9     CONTINUE                                                      00032110
      DO 885 I = 1,5                                                00032120
      JLOW = (I - 1) * 10 + 1                                       00032130
C     JLOW = 1,11,.....41                                          00032140
      JUP = JLOW + 9                                                00032150
```

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C        JUP = 10,20,....50                                      00032160
         IF (KMAD(IH1,JLOW) .LE. 0) GO TO 886                    00032170
C YET ANOTHER MOD TO TLPRNT                                      00032180
C                              WFH RTI 10/1/78                   00032190
         DO 731 IK=1,50                                          00032200
   731 KSTOR(IK)=KMAD(IH1,IK)                                    00032210
         CALL TLPRNT(6,KSTOR,PKHIST,XY,XY,XY,JLOW,JUP,1)         00032220
C        WRITE(IPTR2,5100) (KMAD(IH1,K), K = JLOW,JUP)           00032230
885    CONTINUE                                                  00032240
886    CONTINUE                                                  00032250
888    CONTINUE                                                  00032260
         NM(M3)=NMAX                                             00032270
C        SAVE NUMBER OF MASSES MAXIMIZING                        00032280
         RETURN                                                  00032290
C5000 FORMAT(//,' SINGLET MASSES CONTRIBUTING TO DETECTED SPEC. (MAXIMUM00032300
C     * OF 50 PRINTED) '/)                                       00032310
C5100 FORMAT(10(2X,I3))                                          00032320
         END                                                     00032330
C :    THIS ROUTINE DOES ALL PRINTING FOR CLEANUP.  PLEASE USE IT TO ADD 00032340
C :    NEW PRINTING IN ANY SUBROUTINE.                          00032350
C \      THE CALL STATEMENT ALLOWS FOR PASSING OF ARRAYS         00032360
C       REALS AND INTEGERS.                                     00032370
C       THIS COMPUTER PROGRAM WAS DEVELOPED WITH THE FUNDING SUPPORT 00032380
C       FROM THE NATIONAL INSTITUTES OF HEALTH (GRANTS RR-612 AND 00032390
C       GM-20832) AND THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION 00032400
C       (GRANT NGR-05-020-632).                                 00032410
         SUBROUTINE TLPRNT(N,IAR,AR,R1,R2,R3,I1,I2,I3)          00032420
         INTEGER N,I1,I2,I3,IONE,NINE,IP/0/                     00032430
         REAL R1,R2,R3                                          00032440
         DIMENSION IAR(1),AR(1)                                 00032450
         COMMON /DUBBUG/IFLAG                                   00032460
         COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT         00032470
         DATA IONE,NINE/1,9/                                    00032480
C       IFLAG IS RESET IF NO PRINTING IS TO BE DONE/            00032490
C       IF (IFLAG.EQ.0) RETURN                                 00032500
         GO TO (20,30,40,50,60,70,80) ,N                        00032510
C       THE ABOVE IS A CASE STATEMENT FOR EXECUTING PRINT      00032520
C20       WRITE(IPTR2,515)                                      00032530
   20 IF(IFLAG.EQ.0)RETURN                                      00032540
         WRITE(IPTR2,520) I1,I2,I3                              00032550
C....WRITE TO TERMINAL                                          00032560
         IF(IP.EQ.1)RETURN                                      00032570
C       IF(IP.EQ.1)GO TO 21                                    00032580
C THE WRITE TO UNIT 7 STATEMENTS WERE DETERMINED TO BE          00032590
C SUPERFLUOUS AND WERE COMMENTED OUT 3/30/78 -                  00032600
C                              WFH                              00032610
C       WRITE(7,521)                                           00032620
         IP=1                                                   00032640
C 21   WRITE(7,22)I1                                            00032650
C 22   FORMAT(I6)                                               00032660
C       THIS DOES TLOC STUFF                                   00032670
         RETURN                                                 00032680
   30 IF(IFLAG.EQ.0)RETURN                                      00032690
         WRITE(IPTR2,1400)                                      00032700
         WRITE(IPTR2,530) (IAR(I),I=IONE,NINE)                  00032710
C       ABOVE WRITES NPHIST                                    00032720
         WRITE(IPTR2,535) (AR(I),I=IONE,NINE)                   00032730
C       ABOVE WRITES PKHIST                                    00032740
```

```
        RETURN                                                      00032750
C515     FORMAT(/,10('-------'))                                    00032760
520     FORMAT(1H1,1X,'   ***** SPECTRUM DETECTED *****',/,         00032770
      -/' SPECTRUM NO. IS ',I5,'.   LEFT AND RIGHT HISTOGRAM BOUNDS ', 00032780
      -'ARE ',I5,' AND',I5,'.'/)                                    00032790
530     FORMAT(/,' PEAK HIST   ',/,8X,9I6,//' ION CURRENT HIST ')   00032800
535     FORMAT(1X,9F9.0)                                            00032810
1400    FORMAT(' HISTOGRAM POSITIONS 1 - 9 ...'/)                   00032820
C THESE MODS HAVE BEEN ADDED WITH ADDITIONAL STATEMENTS (WRITE)     00032830
C BEING INCORPORATED IN TLOC                                        00032840
C                                       WFH RTI 9/31/78             00032850
                                                                    00032860
   40   WRITE(IPTR2,31)                                             00032860
   31   FORMAT(' ***FATAL READ ERROR ON MAIN INPUT FILE IN TLOC***') 00032870
        RETURN                                                      00032880
   50   IF(IFLAG.EQ.0)RETURN                                        00032890
        WRITE(IPTR2,32) I1,R1                                       00032900
32      FORMAT(' SPEC. REJECTED FOR MIN. RATE. SPEC = ',I6/'  RATE = ',F10 00032910
      *.3/)                                                         00032920
        RETURN                                                      00032930
   60   IF(IFLAG.EQ.0)RETURN                                        00032940
        WRITE(IPTR2,5000)                                           00032950
5000    FORMAT(//,' SINGLET MASSES CONTRIBUTING TO DETECTED SPEC. (MAXIMUM 00032960
      * OF 50 PRINTED) '/)                                          00032970
        RETURN                                                      00032980
C                                           .                       00032990
   70   IF(IFLAG.EQ.0)RETURN                                        00033000
        WRITE(IPTR2,5100)(IAR(I),I=I1,I2)                           00033010
5100    FORMAT(10(2X,I3))                                           00033020
        RETURN                                                      00033030
C                                                                   00033040
   80   WRITE(IPTR2,55)                                             00033050
   55   FORMAT(1X,'INCORRECT NUMBER OF RECORDS SPECIFIED - ',       00033060
      1'EXECUTION NOT AFFECTED')                                    00033070
        RETURN                                                      00033080
        END                                                         00033090
        SUBROUTINE XTREM(ARRAY,NPTS,XMIN,MININD,XMAX,MAXIND)        00033100
        INTEGER ARRAY(411),XMIN,MININD,XMAX,MAXIND                  00033110
        XMIN=ARRAY(1)                                               00033120
        XMAX=ARRAY(1)                                               00033130
        MININD=1                                                    00033140
        MAXIND=1                                                    00033150
        IF(NPTS.LE.1)RETURN                                         00033160
        DO 2 I=2,NPTS                                               00033170
        IF(ARRAY(I).GE.XMIN)GO TO 1                                 00033180
        XMIN=ARRAY(I)                                               00033190
        MININD=I                                                    00033200
        GO TO 2                                                     00033210
1       IF(ARRAY(I).LE.XMAX)GO TO 2                                 00033220
        XMAX=ARRAY(I)                                               00033230
        MAXIND=I                                                    00033240
2       CONTINUE                                                    00033250
        RETURN                                                      00033260
        END                                                         00033270
        SUBROUTINE OPNFIL                                           00033280
        INTEGER CLNFLG                                              00033290
        INTEGER MASBUF(6),VALBUF(6),AJACEN,AHEAD,ISQ(1000)          00033300
        INTEGER NAME,RDATE,BITMAP,GCTIME,LIBMAP,INTEG,LOMASS,MAD,ADS 00033310
        INTEGER HIMASS,POINTS,TAPCNT,MAXSP,LSTCNT,DEVICE,SPCNO      00033320
```

```
      INTEGER LSTMIN,SPEC,IND,IR,BK,NM,NTM,PNAME(32)              00033330
      INTEGER HIST(10),UNIT,NNAME(18),IRNO                        00033340
      INTEGER NUSPEC,NMASS,OVLAP,EXPNAM,SRLIB(5),SECOND           00033350
      INTEGER QDUBLT,QSATS,NLINE,RAWBUF,FSTPGE,FSTREC             00033360
      INTEGER SATLST,SATINX,PASS1,ITOM,EOF                        00033370
      INTEGER GPEAK,SPARE1,SPARE2,SPARE3,SPARE4,SPARE7            00033380
      INTEGER*4 TIMREM,TIMCNT                                     00033390
      REAL     SPARE5,SPARE6                                      00033400
      REAL     ISVP8,ISVP9                                        00033410
      REAL     QNORM                                              00033420
      REAL*8    C4,C1,C2,SGX,SHX                                  00033430
      DIMENSION G(9),H(11),GNU(18),HNU(18)                       00033440
      COMMON PKHIST(20),NPHIST(20)                                00033450
      COMMON YM5,YM4,YM3,YM2,YM1,Y0,YP1,YP2,YP3,YP4,YP5           00033460
      COMMON GM4,GM3,GM2,GM1,G0,GP1,GP2,GP3,GP4                   00033470
      COMMON SG,SG2,SIG,S1,S12,AN,AA,BB,CC,DD                     00033480
      COMMON NAME(32),RDATE(5),BITMAP(64),GCTIME                  00033490
      COMMON LIBMAP(17),INTEG,LOMASS,HIMASS,POINTS,TAPCNT         00033500
      COMMON MAXSP,LSTCNT,DEVICE(5),SPCNO                         00033510
      COMMON SPEC(14,411),IND(3,411),NUSPEC(411),NMASS            00033520
      COMMON RMAX(3),IR(3),BK(3),NM(3),NTM(3),GPEAK(3,11)         00033530
      COMMON SPARE1,SPARE2,SPARE3,SPARE4,SPARE5,SPARE6,SPARE7     00033540
      COMMON RATMIN,RATEMX,SIGY0,SIGNXT,SIGLST                    00033550
      COMMON ISVN8,ISVN9,ISVP8,ISVP9,SIGMA7,SATVAL,SATMAX         00033560
      COMMON MODE1,MODE2,NLWCUT,NUPCUT,SATPKS(25),NSAT,EXPNAM(5)  00033570
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT              00033580
C THIS COMPRISES THE FIRST OF SIX SUBROUTINES FOR THE EPA I/O    00033590
C INTERFACE TO THE CLEANUP PROGRAM. IN THE RTI SYSTEM, THE       00033600
C PRIMARY INPUT AND OUTPUT FILES WOULD BE OPENED HERE. FOR EPA   00033610
C ONLY A DUMMY RETURN IS NECESSARY.                              00033620
C                                            WM.F.HARGROVE       00033630
C                                            RTI 11/25/78        00033640
      EQUIVALENCE (RSEC,ISEC)                                     00033650
C NOW PICK UP SATURATION VALUE FROM TTY...                       00033660
      WRITE(IPTR1,3110)                                           00033670
 3110 FORMAT(1X,'ENTER SATURATION VALUE IN F6.0:')               00033680
      READ(IRDR,3112) SATVAL                                      00033690
 3112 FORMAT(F6.0)                                                00033700
      WRITE(IPTR1,3113) SATVAL                                    00033710
 3113 FORMAT(1X,'SATVAL= ',F8.1)                                  00033720
      RETURN                                                      00033730
      END                                                         00033740
      SUBROUTINE CLSFIL                                           00033750
C THIS COMPRISES THE SECOND OF SIX SUBROUTINES FOR THE EPA I/O   00033760
C INTERFACE TO THE CLEANUP PROGRAM. IN THE SYSTEM, THE           00033770
C PRIMARY INPUT AND OUTPUT FILES WOULD BE CLOSED HERE. FOR EPA   00033780
C ONLY A DUMMY RETURN IS NECESSARY.                              00033790
C                                            WM.F.HARGROVE       00033800
C                                            RTI 11/25/78        00033810
      RETURN                                                      00033820
      END                                                         00033830
      SUBROUTINE CLSRUN(ISQ,MU)                                   00033840
C THIS COMPRISES THE THIRD OF SIX SUBROUTINES FOR THE EPA I/O    00033850
C INTERFACE TO THE CLEANUP PROGRAM. IN THE RTI SYSTEM, THE       00033860
C FIRST, LAST, AND NUMBER OF SCANS WOULD BE INSERTED INTO THE HEADER  00033870
C RECORD WHICH WOULD THEN BE WRITTEN OUT. FOR EPA ALL THAT IS NEEDED  00033880
C IS A RETURN.                                                   00033890
      INTEGER MU,ISQ(1000)                                        00033900
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          RETURN                                                      00033910
          END                                                         00033920
          SUBROUTINE OPNRUN(LIBBLK,IEOF)                              00033930
C THIS COMPRISES THE FOURTH OF SIX SUBROUTINES FOR THE EPA I/O INTERFACE00033940
C TO THE CLEANUP PROGRAM. THE HEADER RECORDS ARE READ IN              00033950
C AND WRITTEN OUT AGAIN AND THE CIRCULAR QUEUE FOR KEEPING TRACK OF SCAN00033960
C TIMES IS INITIALIZED. THE MAIN DIFFERENCE BETWEEN EPA'S OPNRUN AND  00033970
C RTI'S OPNRUN IS THAT HERE FOR EPA SATVAL IS READ IN FROM THE TTY,   00033980
C WHEREAS RTI'S SETUP PICKS IT OFF THE RUN HEADER RECORD.             00033990
C                                                    WM.F.HARGROVE    00034000
C                                                    RTI 11/25/78     00034010
C                                                                     00034020
          INTEGER LIBBLK(1024),EOF,NS                                 00034020
          INTEGER IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT,IEOF,ISEC           00034030
          REAL SATVAL,SECSCN,RSEC                                     00034040
          INTEGER NAME(3),HDRFLG,DATE(2),RUNHDR,RUNMIN,               00034050
         1SAMPID(16),INAM(2),RUNCON(16),BUF4(11),LOPMAS,HIPMAS,       00034060
         2RETMIN(14),RETSEC(14),BLANK/'    '/,INCOS(2)/'INCO','S   '/ 00034070
          COMMON /HDR1/ NAME,HDRFLG,DATE,RUNHDR,RUNMIN                00034080
          COMMON /HDR2/ SAMPID,INAM                                   00034090
          COMMON /HDR3/ RUNCON,SECSCN                                 00034100
          COMMON /HDR4/ BUF4,LOPMAS,HIPMAS                            00034110
          COMMON /FLAGS/ EOF                                          00034120
C                                                                     00034130
          COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT              00034140
          COMMON /CQUEUE/ RETMIN,RETSEC,NS                            00034150
C INITIALIZE CIRCULAR QUEUE FOR SAVING SCAN TIMES                     00034160
          NS=0                                                        00034170
C HAND CONTROL TO PADDOCK                                             00034180
          CALL EPAHDR                                                 00034190
          IEOF=EOF                                                    00034200
          IF(IEOF.EQ.1)RETURN                                         00034210
C NOW PUT THINGS IN THEIR APPROPRIATE PLACES FOR CLEANUP              00034220
          IF(HDRFLG.EQ.0)GO TO 10                                     00034230
          WRITE(IPTR1,20)                                             00034240
   20     FORMAT(1X,'*** EXEXUTION TERMINATING, INCORRECT FORMAT OF HEADER00034250
         1RECORD DETECTED AT BEGINNING OF FILE IN OPNFIL***')         00034260
          STOP                                                        00034270
C NOW PICK UP DATE                                                    00034280
   10     CONTINUE                                                    00034290
          DO 30 I=1,2                                                 00034300
   30     LIBBLK(I+30)=DATE(I)                                        00034310
C SET UP INSTRUMENT NAME                                              00034320
          DO 35 I=10,12                                               00034330
   35     LIBBLK(I)=BLANK                                             00034340
          DO 40 I=1,2                                                 00034350
   40     LIBBLK(I+7)=INCOS(I)                                        00034360
C RUN SAMPLE ID                                                       00034370
          LIBBLK(29)=BLANK                                            00034380
          LIBBLK(30)=BLANK                                            00034390
          DO 50 I=1,16                                                00034400
   50     LIBBLK(I+12)=SAMPID(I)                                      00034410
C REMARKS ON RUN CONDITIONS                                           00034420
          DO 60 I=1,16                                                00034430
   60     LIBBLK(I+137)=RUNCON(I)                                     00034440
          LIBBLK(155)=BLANK                                           00034450
          LIBBLK(154)=BLANK                                           00034460
C PICK UP SCAN RATE                                                   00034470
          RSEC=SECSCN                                                 00034480
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C      LIBBLK(57)=ISEC                                                  00034490
C MOVE IN MASS SCAN RANGE                                              00034500
      LIBBLK(42)=LOPMAS                                                00034510
      LIBBLK(43)=HIPMAS                                                00034520
C SET HDRFLG = FIRST SPECTRUM NUMBER IN RUN                           00034530
      LIBBLK(36)=HDRFLG                                                00034540
C SET MAXIMUM NUMBER OF SPECTRA IN RUN                                00034550
      LIBBLK(38)=100000                                               00034560
      RETURN                                                           00034570
      END                                                             00034580
      SUBROUTINE RDSPC(SPCNO,AVGSPC,I14,IQUPD,IEOF)                   00034590
C THIS COMPRISES THE FIFTH OF SIX SUBROUTINES FOR EPA I/O            00034600
C INTERFACE TO THE CLEANUP PROGRAM. HERE IS WHERE CLEANUP            00034610
C REQUESTS THAT A SCAN RECORD BE READ. ASIDE FROM THE I/O            00034620
C STATEMENTS, THE LOGIC IS THE SAME AS FOR THE RTI LINEAR            00034630
C SYSTEM.                                                             00034640
C                                          WM.F.HARGROVE              00034650
C                                          11/25/78                   00034660
      INTEGER AVGSPC(411),SPCNO,I14,EOF,IEOF                          00034670
      INTEGER INAM(3),ISCN,IDBUF(2),IDHDR,IDMIN,IRTMIN,               00034680
     1IRTSEC,INMBAS,INBUF(411),INSEQ,NIN                               00034690
      INTEGER RETMIN(14),RETSEC(14),NS                                00034700
      REAL IRBAS,IRTIC,CFACT                                          00034710
      INTEGER IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                         00034720
      COMMON /IHDR/ INAM,ISCN,IDBUF,IDHDR,IDMIN,IRTMIN,               00034730
     1IRTSEC,INMBAS,IRBAS,IRTIC                                        00034740
      COMMON /INDATA/ INBUF,INSEQ,NIN                                 00034750
      COMMON /FLAGS/ EOF                                              00034760
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                  00034770
      COMMON /CQUEUE/ RETMIN,RETSEC,NS                                00034780
C HAND THE BALL TO PADDOCK AND GET A RECORD                          00034790
      CALL EPARD                                                      00034800
      IEOF=EOF                                                        00034810
      IF(EOF.LT.2)GO TO 10                                            00034820
      WRITE(IPTR1,20)                                                 00034830
   20 FORMAT(1X,'***EXECUTION TERMINATING DUE TO IMPROPER EOF CONDITION 00034840
     1DETECTED IN RDSPC***')                                          00034850
      STOP                                                            00034860
C CONTINUE WITH NORMAL PROCESSING                                    00034870
   10 IF(EOF.EQ.1)RETURN                                             00034880
C NORMAL SPECTRUM RETRIEVED - GET SCAN NUMBER                        00034890
      SPCNO=ISCN                                                      00034900
C CALCULATE CORRECTION FACTOR                                        00034910
      CFACT=IRBAS/999.0                                              00034920
C NOW SET UP AND LOOP SPEC ARRAY FROM INBUF                          00034930
      DO 60 I=1,411                                                   00034940
   60 AVGSPC(I)=CFACT*INBUF(I)                                       00034950
C UPDATE CIRCULAR QUEUE WHEN NECESSARY                               00034960
      IF(IQUPD.EQ.0)RETURN                                           00034970
      NS=NS+1                                                         00034980
      RETMIN(I14)=IRTMIN                                              00034990
      RETSEC(I14)=IRTSEC                                              00035000
C MISSION ACCOMPLISHED - I HOPE....                                 00035010
      RETURN                                                         00035020
      END                                                           00035030
      SUBROUTINE WRTSPC(SPCNO,NUSPEC,DUBLT,RATE,NPK,TICIN)           00035040
C THIS COMPRISES THE LAST OF SIX SUBROUTINES FOR THE EPA            00035050
C I/O INTERFACE TO THE CLEANUP PROGRAM. THE CLEANED UP SCAN         00035060
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C RECORD IS REFORMATTED AND NECESSARY INFORMATION IS RETRIEVED        00035070
C FROM A CIRCULAR QUEUE. THE LOGIC EXACTLY PARALLELS THAT FOR          00035080
C THE RTI LINEAR ACQUISITION SYSTEM VERSION.                           00035090
C                                              WM.F.HARGROVE           00035100
C                                              RTI 11/26/78            00035110
C                                                                      00035120
      INTEGER SPCNO,NUSPEC(411),DUBLT,NIN,RATE                         00035130
      REAL TICIN                                                       00035140
      INTEGER INAM(3),ISCN,IDBUF(2),IDHDR,IDMIN,IRTMIN,IRTSEC,I7,      00035150
     1INMBAS,INBUF(411),INSEQ,ONAM(3),OSCN,ODBUFF(2),ODHR,            00035160
     2ODMIN,ORTMIN,ORTSEC,ONMBAS,OTBUFF(411),OTSEQ,NOUT,NPK           00035170
      REAL IRBAS,IRTIC,ORBAS,ORTIC,CFACT                               00035180
      INTEGER NS,RETMIN(14),RETSEC(14)                                 
      COMMON /IHDR/ INAM,ISCN,IDBUF,IDHDR,IDMIN,IRTMIN,               00035190
     1IRTSEC,INMBAS,IRBAS,IRTIC                                        00035200
      COMMON /INDATA/ INBUF,INSEQ,NIN                                  00035210
      COMMON /CQUEUE/ RETMIN,RETSEC,NS                                 00035220
      COMMON /OHDR/ ONAM,OSCN,ODBUFF,ODHR,ODMIN,ORTMIN,               00035230
     2ORTSEC,ONMBAS,ORBAS,ORTIC                                        00035240
      COMMON /OTDATA/ OTBUFF,OTSEQ,NOUT                                00035250
      COMMON /UNITS/ IRDR,IPTR1,IPTR2,IPTR3,IIN,IOUT                   00035260
C NOW START FORMING THE HEADER RECORD                                  00035270
      DO 10 I=1,3                                                      00035280
   10 ONAM(I)=INAM(I)                                                  00035290
      OSCN=SPCNO                                                       00035300
      DO 20 I=1,2                                                      00035310
   20 ODBUFF(I)=IDBUF(I)                                               00035320
      ODHR=IDHDR                                                       00035330
      ODMIN=IDMIN                                                      00035340
C RETRIEVE SCAN RETENTION TIMES FROM CIRCULAR QUEUE                    00035350
      I7=NS-7-14*((NS-8)/14)                                           00035360
      ORTMIN=RETMIN(I7)                                                00035370
      ORTSEC=RETSEC(I7)                                                00035380
C FORM OUTPUT ARRAY AND FIND BASE PEAK MASS AND INTENSITY              00035390
C TRANSFER AND DETERMINE NUMBER OF PEAKS AND BASE PEAK                 00035400
      ORBAS=0                                                          00035410
      ONMBAS=0                                                         00035420
      ORTIC=0.0                                                        00035430
      NOUT=0                                                           00035440
      DO 40 I=1,411                                                    00035450
      IF(NUSPEC(I).LE.0)GO TO 30                                       00035460
      ORTIC=ORTIC+NUSPEC(I)                                            00035470
      NOUT=NOUT+1                                                      00035480
   30 CONTINUE                                                         00035490
      IF(NUSPEC(I).LT.ORBAS)GO TO 40                                   00035500
      ORBAS=NUSPEC(I)                                                  00035510
      ONMBAS=I                                                         00035520
   40 CONTINUE                                                         00035530
      ONMBAS=ONMBAS+39                                                 00035540
C CALCULATE CORRECTION FACTOR                                          00035550
      IF(ORBAS.GT.0)GO TO 50                                           00035560
      WRITE(IPTR2,45) SPCNO                                            00035570
   45 FORMAT('-',/' *** WARNING - 0 BASE PEAK IN WRTSPC, SCAN #',I5,' ***')00035580
      RETURN                                                           00035590
C CALCULATE CORRECTION FACTOR                                          00035600
   50 CFACT=999.0/ORBAS                                                00035610
C NORMALIZE SPECTRUM                                                   00035620
      DO 60 I=1,411                                                    00035630
```

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   60 OTBUFF(I)=CFACT*NUSPEC(I)+.05              00035640
C NOW EVERYTHING IS READY FOR PADDOCK'S OUTPUT ROUTINE    00035650
      CALL EPAWRT                                00035660
      RETURN                                     00035670
      END                                        00035680
```

APPENDIX B

"EXTRACTION OF MASS SPECTRA FREE OF BACKGROUND AND NEIGHBORING COMPONENT
CONTRIBUTION FROM GAS CHROMATOGRAPHY MASS SPECTROMETRY DATA"
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Extraction of Mass Spectra Free of Background and Neighboring Component Contributions from Gas Chromatography/Mass Spectrometry Data

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An effective, minicomputer-based method is described for systematically extracting resolved mass spectra of mixture components from GC/MS data. Using tabular peak models derived directly from the raw data, the spectra have column bleed background removed and are corrected for interference from neighboring elutants and peak saturation. Individual components are detected in the data by means of a pair of histograms which statistically characterize the positions of mass fragmentogram peak modes. These data-adaptive corrections avoid costly iterative numerical procedures and allow obtaining representative mass spectra from GC/MS data of complex mixtures on a routine basis. Using this approach, components that elute within less than two spectral scan times of each other can be detected and their mass spectra well resolved.

With the increasing application of gas chromatography/ mass spectrometry (GC/MS) systems to mixture component identification in biomedical research (1, 2) and other areas (3), it has become important to be able to systematically isolate and identify minor components in the complex mixtures being analyzed. Because of instrumentation limitations, the mass
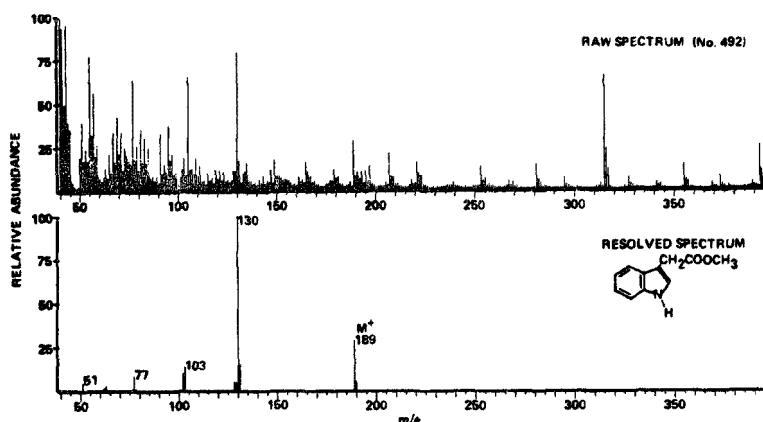
Figure 1. (a) Spectrum of indole acetic acid 3-methyl ester from a GC/MS analysis of human urine before processing. (b) Resolved spectrum of indole acetic acid 3-methyl ester

spectra obtained from a GC/MS analysis of a complex mixture are often markedly different from the spectra of the corresponding pure compounds. Differences may be caused by contributions from unresolved neighboring components during partial separation and also from GC septum and column bleed. These extraneous contributions may severely distort the relative intensities of ions in the mass spectrum of a particular component as well as contribute peaks that are not characteristic of the component being examined. Characterization and removal of these spurious ion contributions is especially important in the analysis of minor constituents where the mass spectra of interest may be substantially masked or distorted.

Our objective has been to implement a solution to these problems which is general and can systematically and reliably resolve GC/MS data with a minimum of human intervention. At the same time we have constrained the design so that the programs can run on a laboratory minicomputer. The first of these objectives has necessitated the use of a relatively complex mathematical treatment of the GC peak profile analyses as compared to that previously reported by Biller and Biemann (4). Both the present approach and that of Ref. 4 are based on analyses of mass fragmentogram profiles (4-6), a method which has been in use in various laboratories including our own, for a number of years. The method described here, however, differs substantially in the extraction of information from the profiles and thereby avoids several serious limitations inherent in the system described previously (4). By using tabular models of the elutant peak shapes together with a polynomial approximation to the GC background, and by deploying the elutant location and multiplicity information gained in analyzing individual fragmentogram profiles to assist in analyzing the others, we can achieve significant advantages in the quality of the reduced data. These include better final GC resolution, the proper assignment of ions to resolved elutant spectra (whether or not they are shared between neighboring components), more accurate spectral amplitudes free from background contributions, and the recovery of usable information from distorted data as in saturated peaks. We feel these improvements are important to a system which can reliably extract component spectra of sufficiently high quality from GC/MS runs to enable more definitive library matching, easier human interpretation of unknowns, and even the addition of extracted spectra to a library as authentic spectra. In our experience, these are essential assets for a GC/MS data system which is to be routinely

applied in medical research and amply justify the complexity of the analysis.

EXPERIMENTAL

The GC/MS computer system used in this investigation consists of a Finnigan 1015 Quadrupole mass spectrometer interfaced to a PDP-11/20 minicomputer system for data acquisition. In one frequent mode of operation a complete mass scan (from mass 40 to 450) is completed each 3.7 s and 600 consecutive mass spectra are collected during a typical GC/MS analysis. Our initial experience of comparing the experimental mass spectra from a complex GC/MS analysis with a library of known mass spectra produced very poor results because of contamination of the experimental data by spectra of column bleed and of neighboring, unresolved components. Tolerable matches were only achieved when a component was present in large quantity in the GC/MS analysis. In order to overcome these problems, we have developed a computer program capable of systematically extracting from the raw GC/MS data, spectra representative of the pure elutant compounds.

The raw mass spectrum (Figure 1a) of indole acetic acid 3-methyl ester obtained from a GC/MS analysis of the acidic fraction (after methylation) of human urine typifies this situation. This component elutes at or near spectrum number 492 in the total ion plot (TIC) shown in Figure 2. Closer examination of Figure 2 shows that this component is submerged both in mass spectral contributions from neighboring components and background from GC column bleed. For comparison, a library spectrum (7) of indole acetic acid 3-methyl ester is shown in Figure 3. Figure 1b shows how, after processing the raw GC/MS data by the method described below, we can retrieve a high quality mass spectrum of indole acetic acid 3-methyl ester free from the environmental perturbations present in Figure 1a.

Thus, in the systematic analysis of GC/MS data the problem is first to detect where in the GC trace each component shows its maximum ion intensity and then to extract from these regions representative spectra for each of the detected components. The extracted mass spectra should be as free as possible from intensity distortions relative to their library counterparts, and from the presence of extraneous ions (e.g., peaks from either neighboring components or gas chromatographic column bleed).

DESCRIPTION OF METHOD

To obtain a reliable solution to these problems, it is necessary to analyze a number of spectra on either side of the ion current maximum for each elutant. A basic assumption of our approach is that the mass spectra of two neighboring unresolved elutants can be distinguished; that is, there exist some masses for which ions occur in the mass spectrum of one component but not in the other and vice versa. A schematic representation for two closely spaced elutants is given in Figure 4. By locating the "resolved" or singlet fragmentogram peaks at such masses (detected on the basis of profile mor-

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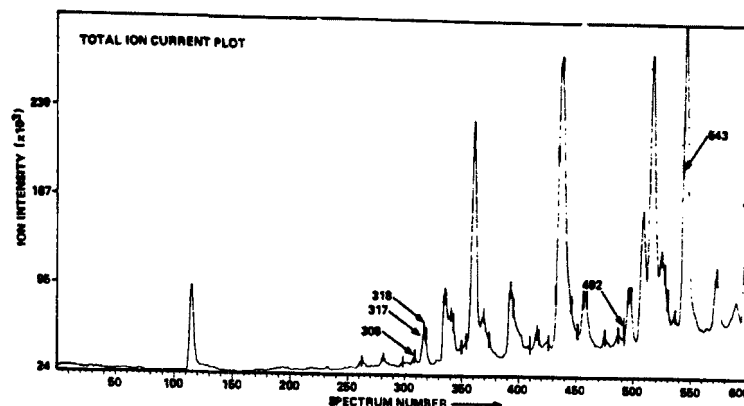
Figure 2. Total ion current plot for a GC/MS analysis of a urine sample. Components were found at vertical bar marks on TIC
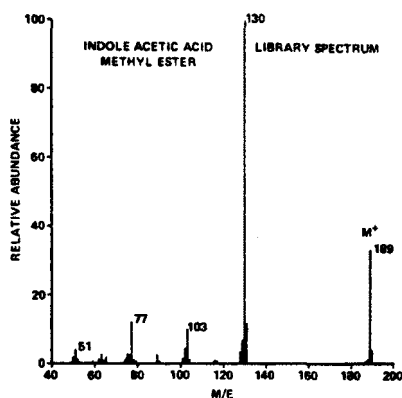
Figure 3. Mass spectrum of indole acetic acid 3-methyl ester taken from a library of biological compounds

Figure 4. A schematic representation of the set of partial mass fragmentograms for two closely spaced elutants. Components A and B have some masses in common

phology), one can infer directly the positions of the elutants present and derive tabular models of the individual peak shapes. These models can be used subsequently to separate the unresolved fragmentogram complexes. The use of tabular peak models derived from the data itself accurately accommodates the a priori unknown peak profiles of particular elutants without solving for multiparameter, nonlinear model functions. Since the data are sampled often enough to satisfy the sampling theorem (8), these tabular models contain the necessary information to reconstruct a continuous peak envelope and can therefore be used as if they were continuous analytical models. For the typical peak shapes encountered, the collection of 5–10 mass spectra per singlet elutant peak represents a sampling frequency greater than twice the Fourier bandwidth of the peak. In addition, the mass by mass analysis of the fragmentogram peak complexes facilitates the mass dependent subtraction of background. (The large variation in background levels for different masses is a function of both the type of GC column used and the mixture being analyzed.)

By addressing the problem in this way, we have been able to produce accurate intensity information for the processed mass spectra and simultaneously distinguish with greater confidence which masses contribute to particular elutant spectra. We have been able to distinguish reliably elutants coming off within one and a half to two spectral scan times of each other. The succeeding sections discuss in more detail the

procedures used to detect and resolve the mass spectra of unique elutants.

Detection of Elutants in GC/MS Data. Elutant detection involves finding the location of each mixture component in the GC/MS data, even if it does not have a corresponding peak maximum in the overall total ion current trace. Ideally for a given elutant, the fragmentograms for all its ion masses will show maxima at the same time and, in practice, this holds for well-resolved materials. However, for partially resolved mixtures, the complicating factors of peak overlap and background contributions can caus- fragmentogram maxima for neighboring components to show significant variation in their positions on the time axis. Reliable position information for each elutant is best derived from the fragmentogram profiles containing singlet peaks for that elutant, that is, from fragmentograms at those spectral masses unique to the elutant relative to its neighbors.

The approach used for elutant detection is to compute two histograms of candidate singlet peak positions and to select as elutant locations significant histogram maxima. The first histogram measures the number of singlet mass fragmentogram profiles which reach maxima in each time interval. The second histogram measures the total singlet ion intensity above background at these maxima. These two types of histogram contribute complementary information for judging elutant locations. At a given elution time, the histograms include fragmentogram peak maxima from all masses over seven spectra. The position of each maximum is determined by a parabolic least squares interpolation about the top five points in the sampled peak data. If the intensities of the five points contributing to the maximum are Y_{-2}, Y_{-1}, Y_0, Y_1, and Y_2, then the expression for the time coordinate of the maximum is

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$$t = \frac{7(2Y_{-2} + Y_{-1} - Y_1 - 2Y_2)}{10(2Y_{-2} - Y_{-1} - 2Y_0 - Y_1 + 2Y_2)}$$

The time coordinates of maxima are estimated to one third of the time to collect each spectrum in order to separate very close neighbors. Because we measure peak locations to one third of a spectral scan time, appropriate shifts are also included to account for the fact that higher masses are measured later in each spectral scan than lower masses. To build these histograms, the program examines the profiles of each mass fragmentogram in the data. Only peaks with intensities above a prescribed threshold are added into their appropriate time positions in the histograms. Peaks that are obvious multiplets (multiple extrema) are not incorporated into the histograms but are marked for later resolution. After all of the histogram information is collected for a given region, components are defined to be detected at locations where both the intensity and peak count histograms show maxima that are above a threshold. This statistical approach, looking for "clusters" of fragmentogram peaks in the histograms, does not depend upon a correct decision for each peak but rather on a preponderance of good decisions looking over all of the data. It will fail to resolve elutants very close together which do not have enough distinguishing mass spectral components as described above. In general, however, using this approach we are able to detect and resolve spectra reliably that elute with a separation in time as small as one and a half to two spectral scan times. (Two scan times correspond to 25% of a typical GC peak width at the scan rate we use.) Elutants this close often do not show multiple extrema in the fragmentogram profiles of masses common to both spectra and could not be separated properly except for this type of procedure. If two elutants are separated by less than 1.5 scan times, resolution becomes less certain depending on their relative concentrations and mass spectral distinctness.

Estimation of Spectral Intensities and Background for Well Resolved Elutants. Once the locations of elutants in the GC effluent have been determined, we proceed to compute a resolved spectrum for each material. To illustrate the principles involved in spectral amplitude and background estimation, we consider the simple case of an elutant that is well separated in time from its nearest neighbors. This analysis will be extended to the more complicated case of multiplet resolution in a later section. By "well-separated" we imply only that there are no maxima in the elutant detection histograms for three or four spectra on either side of the elutant under consideration. In such a situation, each of the mass fragmentogram profiles in the vicinity of the elutant will consist of a background on which is superimposed a peak with amplitude representative of the elutant spectral component at that mass. The background (contributed by both GC column bleed and possible tailing from nearby, high-concentration elutants) is distinguished from the elutant peak by the fact that it varies much more slowly with time. Reasonable estimates can be made by assuming that, for any particular mass fragmentogram, the background amplitude varies at most linearly with elution time in the vicinity of a given elutant. This approach to background determination, using the actual fragmentogram characteristics around each elutant, automatically tracks changes in the bleed levels observed during a run. It should be noted that our model is a first-order approximation subject to some error. A more accurate approximation would involve representing the background variations over a larger span of spectral scans than we are able to manage with the current program organization and computer memory limitations. We feel that the linear estimate is justified, however, in that it produces results within the error limits from other data uncertainties.

To complete the estimation process, we use a model peak

to determine the contribution of each mass fragmentogram to the elutant spectrum. Much work has been done on the analytic approximation of gas chromatographic peak shapes (9, 10). Our experience has been that relatively simple models do not adequately approximate the range of shapes encountered and more complex models require large amounts of computing to determine model parameters. Noting that a separate model must be developed for each elutant and with a view toward obtaining the peak shape and definition necessary for multiplet resolution within reasonable computing resources, we have approached the problem by using tabular peak models taken from the data itself. Such models, defined at discrete sample points, can be evaluated at any required intermediate point by interpolation (since the sampling theorem is satisfied) and automatically reflect any peak asymmetries which may be present. For a given elutant, the model will be independent of mass, assuming that relative molecular fragmentation probabilities do not change with elutant pressure within the mass spectrometer. A number of criteria should be satisfied by the tabulated model peaks. They should be singlet peaks superimposed on as small a background as possible and they should be relatively intense in order to ensure a good signal-to-noise ratio and good definition of peak skirts.

Candidate singlet peaks may be distinguished from doublet or background peaks by the feature that they are relatively sharp. One way to measure peak "sharpness" is to use a logarithmic rate function defined as follows:

$$\text{rate} = \sum_{t=1}^{3} \left[\frac{(Y_{t-1} - Y_t)}{Y_t} + \frac{(Y_{-(t-1)} - Y_{-t})}{Y_{-t}} \right]$$

where the Y_t are evaluated at equal scan widths at each side of the mode of the peak. It can be seen that this rate will be large for peaks which are sharp and smaller for peaks which are broad. The rate as defined is also independent of amplitude for peaks of identical shape. A peak with a computed rate below a threshold appropriate to the experimental conditions is considered to be either an artifact of the gas chromatograph (background peak) or a multiplet and is not included in the detection histograms.

During the process of computing the detection histograms, a list is kept of the unimodal fragmentogram peaks having the highest rate factors in the region under analysis. When a component is detected in a given region, a model peak is then immediately in hand that can be used in the peak height estimation and background removal process. The local minima just on either side of the model peak are used as estimates of the local background (a straight line through the greatest of these minima is removed before the model peak is used for analysis). The selection of the peak with the highest rate factor as our model peak has worked well in producing models which are singlets and suffer least from interference by background and neighboring fragmentogram peaks.

Given the fragmentogram peak model for this case of a well-separated elutant, we can now correct the individual mass fragmentograms for background and estimate true mass spectral intensities for the elutant. For the fragmentograms exhibiting peak maxima "near" the location of this elutant (see below for detailed selection criteria), each peak in the set is quadratically interpolated to align it on a common time origin (this removes the time shift between collection of low and high mass data). This is done by fitting a parabola through successive groups of three points near the peak mode and interpolating to give four equally spaced points about the mode, separated by one spectral scan time. With the peaks in this standard form, they are ready for the least squares analysis below. Assuming a linear background model over the region of 5 to 10 scan intervals under consideration, the local background B_t at time t is approximated by

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$$B_t \sim c + dt$$

where c is the background offset and d is its slope. The interpolated elutant peak model is normalized to unit area and has amplitudes P_t at times t. Then for a given mass fragmentogram, the amplitude of the actual fragmentogram profile Y_t at time t can be approximated by

$$Y_t \sim pP_t + (c + dt)$$

where p measures the elutant amplitude above background. Note that this model assumes a superposition principle based on the earlier assumption of constant relative fragmentation probabilities and a linear encoding of ion current information. If ion current data are obtained from nonlinear electronic systems or read from film, the peak model itself would be amplitude dependent and this linear analysis could not be applied until appropriate amplitude linearization corrections were made. From the above model, we can derive a least squares estimate for the elutant amplitude p and the background parameters c and d by minimizing the error function

$$E = \sum (Y_t - pP_t - c - dt)^2$$

according to the conditions

$$\frac{\partial E}{\partial p} = \frac{\partial E}{\partial c} = \frac{\partial E}{\partial d} = 0$$

The summation in the error function is over all available points in the peak profile as well as the neighboring background points within the window of scans contained in the computer's memory. These conditions yield three linear equations in the three parameters which can be solved by standard techniques (11). From the solution of these equations for the value of p, we get the spectral intensity for the mass under consideration. This analysis is applied to all mass fragmentograms with maxima near the elutant location to obtain the complete, intensity-corrected spectrum. It is worth noting that this method, using a tabular model peak derived from the data and elutant locations obtained from the detection histogram analysis, reduces the calculation for each mass spectrum intensity to the solution of a set of linear equations. Specifically, this avoids iterative methods for determining the parameters of a theoretical peak model and for determining elutant time positions.

Fragmentograms are selected for this analysis on the basis of several criteria. Given the nominal elutant position from the detection histogram analysis, a fragmentogram is excluded (mass spectrum assigned zero intensity) if it has no local peak maximum or if its maximum is displaced from the reference elutant position by more than two thirds of a spectral scan time on either side. Each fragmentogram peak meeting this test must also have an acceptably high rate factor, to be included in the analysis. For peaks of masses greater than 200 amu, we require a rate factor greater than 25% of the rate for the model peak. This restriction is useful for eliminating contributions caused by peaking in column bleed components. In carefully examining GC/MS data sets, we can observe that masses characteristic of the spectra of column bleed components show maxima in their mass fragmentograms just prior (one to two spectra) to the elution of an actual component. In essence, the component appears to "push" the bleed out ahead of itself. Because these peaks are formed by a different process than normal elutant mass fragmentogram peaks, they usually have a much broader shape. Consequently their rate factors will be significantly reduced and they can be eliminated by the rate threshold criterion. The combination of the fragmentogram peak location criterion together with the minimum rate criterion effectively discriminates against extra-

neous contributions to the intensity-corrected spectra without removing authentic mass peaks.

Extraction of Poorly Separated Elutant Spectra. Many instances arise in the analysis of GC/MS data where two or more elutants are poorly resolved by the gas chromatograph. The resulting mass spectra in such a region exhibit ion intensity distortions which reflect the interactions (overlap) between adjacent elutants in addition to the ion contributions of background. The extension of the above procedures to the general case is not difficult. Through the histogram detection and model procedures, one can extract normalized peak models $P, Q, R, \ldots$ for the various elutants present. Then with the assumption of a linear background, the elutant contributions to each fragmentogram profile Y can be estimated by minimizing the error function

$$E = \sum (Y_t - pP_t - qQ_t - rR_t - \ldots - c - dt)^2$$

with respect to the elutant amplitudes $p, q, r, \ldots$, and the background coefficients. Sets of linear equations result for each mass to extract the resolved spectra. In practice, we have not implemented this full procedure beyond the doublet case. Through the following approximations, reasonable results are achievable within available minicomputer resources. Using the histogram method described earlier, neighboring elutants are handled with a "look ahead" procedure. That is, information about an elutant that has just been detected is stored and the detection algorithm is applied to the data in the immediate neighborhood by extending the range over which the detection histograms are calculated. If by including this extended region an additional elutant is detected, we record the position of its mode, select a model peak for this second elutant using the rate criterion, and initiate a doublet resolver algorithm. At present, the extended histograms project four spectral scan widths beyond the position where the first elutant of the multiplet was detected (limited by computer memory). The same criteria are applied as in the singlet case to decide which fragmentogram peaks belong to the pair of detected components. The model used to process the composite fragmentogram peaks (many of which may be singlets belonging to either elutant) assumes that there are two overlapping peaks superimposed on a linear background. The doublet model represents an oversimplification of some situations as, for example, in the case where 3 components elute within a very brief interval. By applying it, however, to successive pairs of elutant peaks (taking first-order account of peak tail contributions from any earlier elutant), it provides acceptable accuracy and peak resolution effectiveness. As indicated above, a fit of the two peak models P and Q with a linear background to the fragmentogram profile Y may be described by the approximation

$$Y_t \sim pP_t + qQ_t + c + dt$$

Minimizing an error function analogous to the earlier singlet case results in 4 linear equations in the peak amplitudes p and q and the background parameters c and d. This set of equations again can be solved by standard methods.

In cases where peaks are actually singlet peaks, the solution should yield zero for the amplitude of the missing component. In practice, for such cases the amplitude of the second component is a very small positive or negative value which is representative of how well the model fits the data. Amplitude results for masses that belong to the second component of the doublet are stored temporarily until this component is moved into the processing window at which time they are incorporated into the analysis of the newly detected component.

Reconstruction of Saturated Peaks in Elutant Spectra. From a practical viewpoint, a fairly common occurrence in
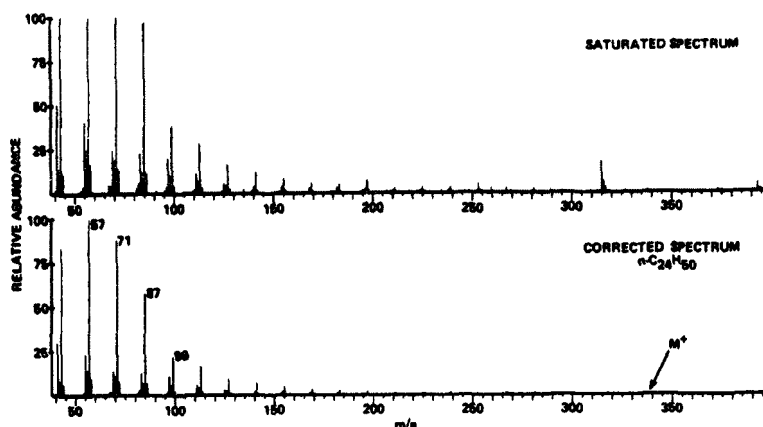
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Figure 5. (a) Saturated unprocessed mass spectrum for tetracosane. (b) Spectrum of tetracosane after processing and correction for saturation

GC/MS data collection systems is the problem of mass peak saturation. Saturated peaks occur when the concentration of a component in the ion source is such that for one or more ion masses the detection system analog-to-digital converter becomes overloaded. Saturated peaks are easily detected because of their characteristic flat tops which have an amplitude determined by the overload limit of the detection system (e.g., the saturation value is 4095 for a twelve-bit analog-to-digital converter).

To obtain accurate amplitudes for component spectra that include saturated mass peaks, we must reconstruct these peaks to estimate their true amplitudes. A convenient way to do this in the singlet case is to use the least squares model that we derived in the preceding sections. To actually apply it for reconstruction of saturated mass fragmentogram peaks, we need to make a small modification to the equations. Instead of summing over all the points in the peak, we sum over only those points that are not saturated in the fragmentogram. As an estimate of the peak mode, we use the mode of the intensity histogram for the component being analyzed. An example of reconstruction of a mass spectrum with saturated ion intensities is given in Figure 5. Figure 5a shows a saturated spectrum of tetracosane (spectrum number 545 in Figure 2) and Figure 5b is the corresponding reconstructed spectrum. It is clear that the reconstructed spectrum will give a far better match with a library spectrum than the saturated spectrum which is badly saturated at masses 43, 57, and 71.

Before leaving the discussion of saturation, we should point out that we have not in practice extended the procedure for saturation correction of singlet peaks to the doublet case as we believe that it would be inadequate for reliable intensity estimates. If too many points are overloaded, there will be insufficient data to accurately estimate the amplitude of each multiplet component. Despite such correction algorithms, there is no substitute for the collection of good quality raw data at the start.

RESULTS AND DISCUSSION

The program based on the algorithm outlined in the preceding sections has been tested on a wide variety of biological samples. It fits comfortably into a DEC PDP 11/45 computer (with 28K words of memory) and takes approximately 8 min to analyze a raw GC/MS data set of 600 mass spectra (scanned from masses 40 to 450). Much of this time is spent in reading the raw data from the disk and other input–output operations. Copies of the program, which is written in FORTRAN, are available from the authors. Currently, this program forms part

of an automated analysis system for the GC/MS analysis of urine and blood samples. The program reduces the raw GC/MS data set of approximately 600 spectra to a set of about 60 resolved elutant spectra which are then matched against a library of mass spectra of biological compounds. This whole process takes about 20 min and produces an analysis of the sample, with known compounds in the mixture identified and the remaining unknown set marked for further study by chemists or other DENDRAL programs (12–14).

In evaluating performance of the program, a major issue is how well it is able to detect elutants in the data. The vertical bars on the TIC (Figure 2) indicate all the places where the program detected and isolated a component from the raw GC/MS data. The program's power of detection is illustrated for example by the elutant detected near spectrum number 492 in the total ion current plot shown in Figure 2. Although there is no evidence of a maximum in the TIC in the region near 492, the program was able to detect and isolate a good quality spectrum of indole acetic acid methyl ester (Figure 1). In the raw data, this spectrum is clearly submerged in background and overlapping contributions. A comparison of the resolved spectrum (Figure 1b) with a library spectrum (Figure 3) shows that the basic spectral intensity profiles are very similar even including the very low intensity ion of mass 89. Some very small ions (of intensity less than 5% relative abundance) are absent from the resolved spectrum because they have been lost in the background noise. It is worth noting that there are no peaks present in the resolved spectrum that are not in the library spectrum, that is, the extraneous mass spectral peaks in the raw data including peaks at masses 105, 253, and 315 are not included in the resolved spectrum. The relative intensities of the mass spectral peaks at masses 51, 62, 65, and 77 have been changed significantly from their levels in the raw data. This illustrates the importance of correcting the intensities for background. The mass spectral peaks at masses 51, 52, 63, 78, and 129 appear to maximize near spectrum 496 in the raw data instead of spectrum 492 because of the overlapping contributions of a poorly resolved elutant. Similar examples of the power of this technique exist in other parts of the GC profile in Figure 2.

The detectability of unresolved elutants is clearly a function of their amplitude relative to neighboring components and background. One way to characterize this is to measure the ratio of the total ion intensity (sum of the mass spectrum amplitudes) in the resolved spectrum compared to that in the unprocessed spectrum including background and overlap effects. The mass spectrum of the processed component at
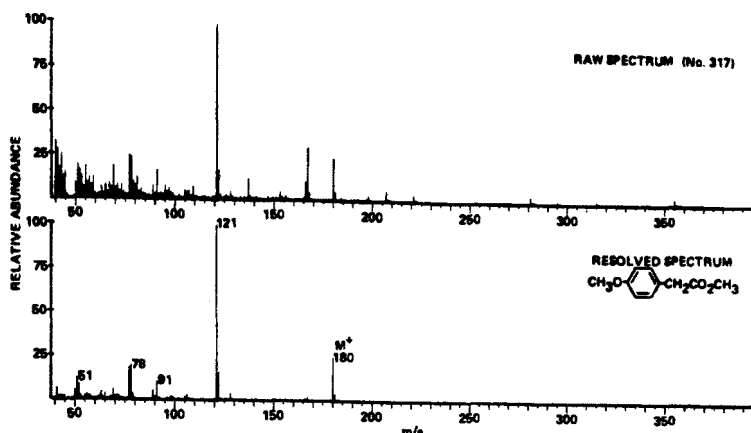
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Figure 6. (a) Mass spectrum of 4-methoxyphenylacetic acid methyl ester before processing. (b) Resolved mass spectrum of 4-methoxyphenylacetic acid methyl ester
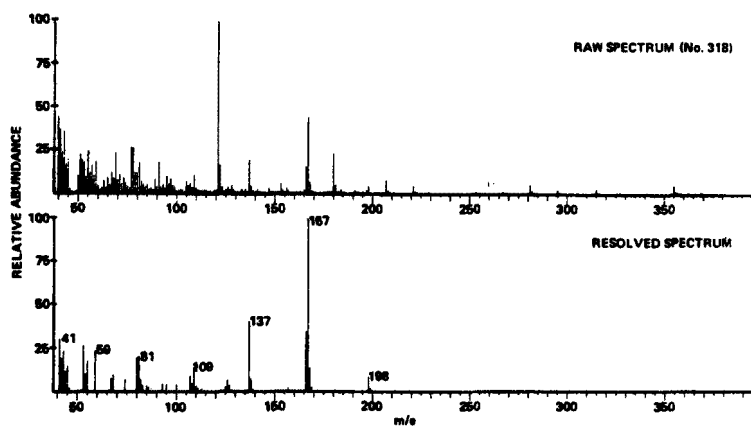

Figure 7. (a) Spectrum of an unknown aromatic ester before processing. (b) Resolved spectrum of unknown ester in Figure 7a

spectrum number 492 comprises only 4% of the total raw ion current. It can be expected that there will be problems detecting components with an ion current ratio that falls much below a level of 4%. Also if two compounds elute within less than 1.5 to 2 spectral scan times of one another, there is an increasing chance that the program will make the wrong decision as to whether there is one or actually two elutants present. Such errors are dependent on the ion current ratio between adjacent elutants, the similarity of their mass spectra, and the stability with which peak positions can be determined.

As an example of doublet resolution, consider the region near spectrum numbers 317 and 318 in Figure 2. The program detects that there are two elutants present and Figures 6 and 7 illustrate the raw and resolved spectra at these locations. The spectrum in Figure 6b is a good representation for 4-methoxyphenylacetic acid methyl ester. The other component is an unknown aromatic ester.

We have evaluated the efficiency of background removal for singlet elutants by examining their mass fragmentograms. After calculating the least squares peak and background levels, we concluded that the computed results are consistent (within 5–10%) with human estimates. They tended to be less accurate for very weak peaks whose shapes were more sensitive to noise distortions.

For the multiplet case, where the peak profiles can be considerably more complex, there is a stronger possibility that

the model will not produce accurate amplitude information. In such cases, as when there are three rather than two elutants present, there is a danger that background contributions will be incorrectly estimated particularly with the limited number of scans that can be held in our minicomputer memory at one time. We feel however that use of a more complex model for triplets is not likely to be able to guarantee much greater precision. A sequential application of the doublet model has produced acceptable results in our experience with the program. Problems most frequently occur when a small amount of an elutant occurs just prior to, or just after, an elutant of high concentration. The intensities of peaks in the small elutant that are common to the large elutant tend to be less accurately calculated than singlet peaks and sometimes may even be discarded as negligible if their intensity relative to the large peak falls much below 10%. This may be especially important for the molecular ions of compounds with the same molecular weight which would be expected to elute near each other.

Comparison with library mass spectra has indicated that correction of intensities for saturated singlet peaks is satisfactory. However, as expected, the accuracy of the calculation decreases as peaks become more heavily saturated. In our case, we are working with model peaks that extend over nine points (i.e., nine scan widths). If more than four of a peak's nine points are saturated, we can expect that its estimated intensity

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will have only limited accuracy because there is insufficient information left to accurately characterize its shape.

Conditions arise in the raw GC/MS data for which it is not possible to extract resolved mass spectra unambiguously. One case is when the elutant-to-background ratio falls significantly below 5%. In these cases, the very weak intensity ions, including isotope ions, usually do not appear in the resolved mass spectra. The other difficulties arise when it is not possible to detect the presence of multiple elutants because they occur within less than one mass spectrum scan time of each other. In this case, the processed spectrum represents the mixture of the two elutants.

In general, we have found that the present system works very well and is capable of detecting and isolating high quality representative mass spectra in GC/MS experiments involving complex biological mixtures.

ACKNOWLEDGMENT

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16. ABSTRACT

Existing computer programs for deconvoluting mass spectrometry data derived from gas chromatography/mass spectrometry/computer systems were evaluated, and the most efficient method was introduced unto an EPA UNIVAC computer. The program chosen was that reported by Rindfleisch and his co-workers at Stanford University. The accompanying program listing is included. The Rindfleisch program was tested with both standard runs and environmental samples. Sample components were successfully identified by an independent computer search program with an accuracy approaching 80%.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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