Computerizing Raw Mass Spectral Data from a Fast-scanning, Single-focusing Mass Spectrometer[1]

H. Y. LI, J. WALDREN, D. ETTER and G. R. WALLER

Oklahoma State University, Stillwater

INTRODUCTION

The development of fast-scanning, single-focusing mass spectrometers has made it possible to acquire a much larger quantity of spectra in a short time. The coupling of the gas chromatograph to the mass spectrometer renders it possible to obtain still larger numbers of spectra and indeed in many instances as many as 180 spectra per hour are taken during the analysis of a complex mixture. Since the manual processing of oscillographic records to provide a line drawing and/or tabular information on m/e intensities is quite time-consuming, it became necessary to computerize the data handling as much as possible. Much time is saved by using the computer and there is also a definite increase in accuracy since human errors are minimized. Second, computer-based data also offers an almost unlimited diversity in operations. Relatively small changes in a program produce the form of output desired. New methods of processing data quickly can be put into operation with the addition of subroutines or

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new programs. Source programs and data are usually compatible or easily convertible to more than one computer so exchanges of information between research centers can be readily done.[2]

A computer-compatible digital data acquisition system for fast-scanning, single-focusing mass spectrometers has been described (Hites and Biemann, 1967); however, the mass spectrometer-gas chromatograph in use at Oklahoma State University (Ryhage, 1967; Waller, 1967) does not presently include any automatic data acquisition system. Consequently the computerization of oscillographic data has been done by manually measuring *m/e* intensity values and introducing these data to the computer on punched cards. A computerized process to present the mass spectrum in both graphical and tabular form is described.

Results and Discussion

The present OSU computing facilities are at two locations. The IBM-7040 in the main computing center does not drive a plotting machine; therefore, processed data must be transferred to the IBM-1620 in the engineering computing center for plotting. Since digital incremental plotters are slow-moving mechanical devices, the most economical way to drive the plotter is by use of a widely available, small, slow computer such as the IBM-1620. Since the computers are housed separately, it is necessary that the program be separated into two parts[3], MSDATA and BARGRF. The former processes the data, while the latter executes the plotting. Figure 1 and 2 show the flow logic of the respective programs.

In program MSDATA, which uses the IBM-7040 computer, the input information may be either normalized data[4], unnormalized background-free data[5], or the raw data containing background[4]. The relationships of the several options on the form of output that may be chosen are shown in Figure 3. The type of data is identified by a code number before each data check. The assigned codes are:

"1" — for background,

"2" — for raw data containing background,

"3" — for background-free unnormalized data,

"4" — for normalized data.

If a background card deck (code 1) and a raw data deck (code 2) are read into the computer successively, the background (code 1) is subtracted from the raw data. In most cases several decks of raw data (code 2) will be processed using the same background before a new background card deck (code 1) is introduced. Any peak that has a higher background value than raw data value will be nullified and later tabulated in an output data sheet giving the background errors related to specific raw *m/e* intensity values. This informs the user that poor raw data or poor background has been used in the computation or mistakes have been

[2]A project under the direction of Dr. Norman Foster and Mr. Mynard Hamming and sponsored by subcommittee E-14 of ASTM is under way for cataloging mass spectrometer computer programs. These computer programs would be made available to other mass spectrometrists.

[3]This dual situation will be improved after installation in late 1968 of the new IBM-360 system in the main computing center.

[4]Data are taken directly from an oscillographic recording in millimeters.

[5]Data are taken directly from an oscillographic recording in relative intensity units.

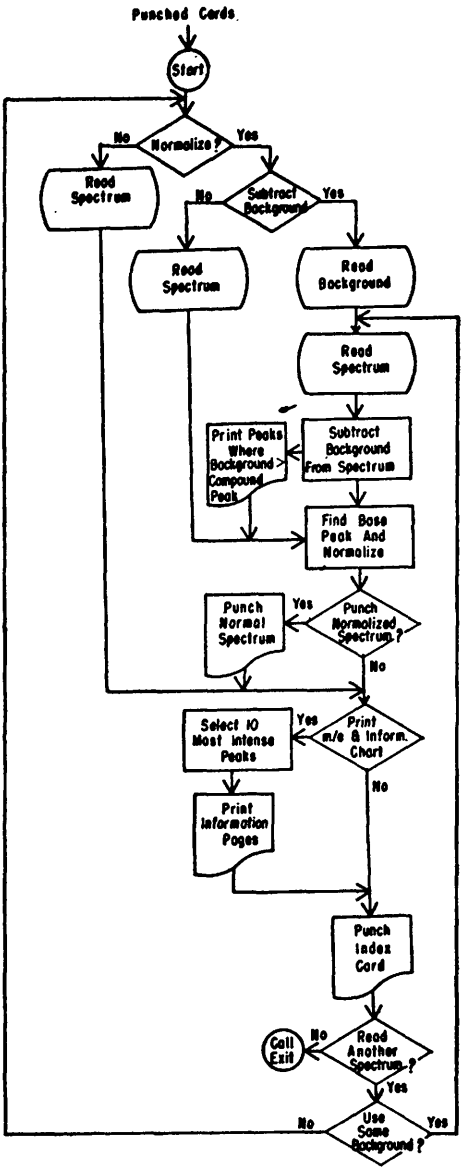

Figure 1. Flow Chart for MSDATA.

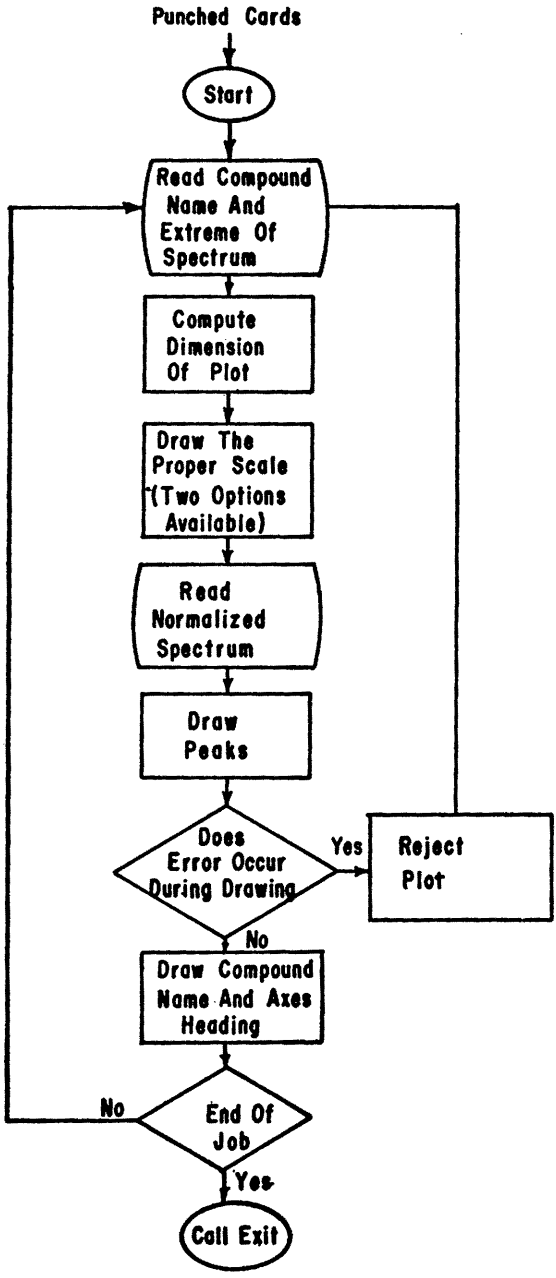

Figure 2. Flow Chart for BARGRF.

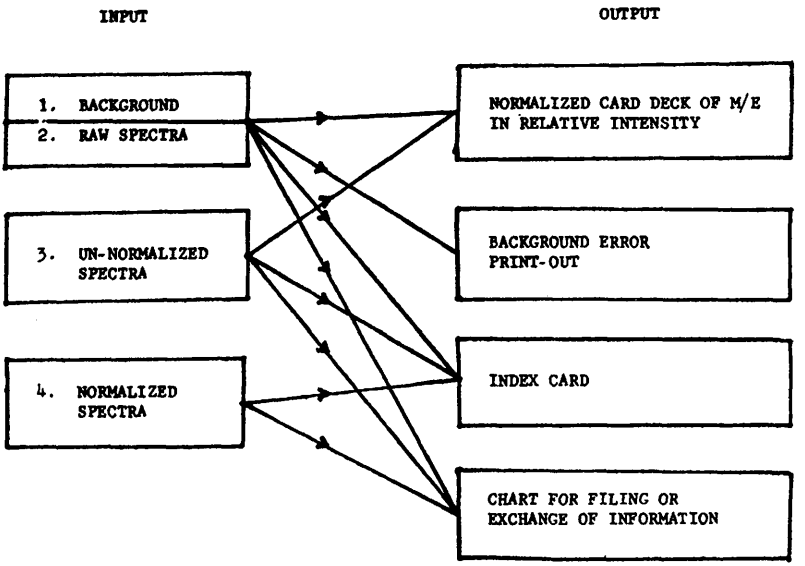

Figure 3. Computer Input-Output Relationships in MSDATA.

made in measuring the spectra. Then he can make a decision whether to rerun the experiment or not. The computer then searches for the base peak (most intense peak of the spectrum), normalizes all the other peaks in percentages of the base peak, ignoring all the zero peaks, and then punches out a normalized data deck for the BARGRF program. If desired, the program will then tabulate the normalized peaks and their relative intensities in a rectangular array (Hamming and Grigsby, 1967) beginning with mass 12 (Figure 4). A separate tabulation of the ten most intense peaks and metastable peaks with relative intensities is also optional (Figure 5).

The normalized data can be transformed into a bar graph by the IBM-1620 computer-Cal Comp 565 plotter combination using program BARGRF. An example is the plot of retinyl acetate shown in Figure 6. The name of the compound and limits (maximum and minimum peaks) of the spectrum are first read in. Dimensions of the bar graph are then computed and the axes and their scales are drawn. At present, two options of the right-hand scale can be chosen by the user: one of these is drawn as percent relative intensity (based on the highest peak, which is arbitrarily assigned a value of 100%) while the other option is in percent sigma (percent of total ionization). The peaks and their relative intensities are then read in and the line drawing is made. If an error is detected during the run or if ink did not flow properly, the operator may reject the present drawing by flipping the Sense Switch 4 on the IBM-1620 console to the "on" position. The program has been designed to draw as many sets of data continuously as one wishes. It has been established that both programs MSDATA and BARGRF provide results which are comparable to manually calculated values and manually performed line drawings.

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PARENT MASS 147

FORMULA C10.H13.N

COMPOUND ACTINIDINE

STRUCTRUAL FORMULA

DR.G.R.WALLER
BIOCHEMISTRY DEPARTMENT
OKLAHOMA STATE UNIVERSITY
STILLWATER, OKLAHOMA

TYPE INLET GAS LIQUID CHROMATOGRAPHY

IONIZATION VOLTAGE 70FV

SOURCE TEMPERATURE 310

SCAN RATE 2 OCTAVES/SEC

SEPARATOR TEMPERATURE 225

COLUMN TEMPERATURE 180

FLASH HEATER TEMPERATURE 210

FLOW RATE 55ML.HE/MIN.

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RELATIVE INTENSITIES OF IONS

M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI	M/E	RI
12	0.0	13	0.0	14	0.0	15	0.0	16	0.0	17	0.0	18	0.0	19	0.0	20	0.0	21	0.0	22	0.0	23	0.0	24	0.0	25	0.0
26	0.0	27	0.0	28	0.0	29	0.0	30	0.0	31	0.0	32	0.0	33	0.0	34	0.0	35	0.0	36	0.0	37	0.0	38	0.0	39	0.0
40	0.0	41	1.0	42	1.5	43	6.0	44	12.0	45	12.0	46	0.0	47	0.0	48	0.0	49	0.0	50	0.0	51	0.0	52	0.0	53	0.0
54	0.0	55	0.0	56	1.0	57	5.0	58	7.0	59	6.0	60	0.0	61	0.0	62	0.0	63	0.0	64	0.0	65	0.0	66	0.0	67	0.0
68	0.0	69	0.0	70	5.0	71	5.0	72	7.0	73	14.0	74	2.0	75	2.0	76	0.0	77	0.0	78	0.0	79	0.0	80	0.0	81	0.0
82	0.0	83	0.0	84	2.0	85	1.0	86	6.0	87	10.0	88	9.0	89	34.0	90	1.0	91	0.0	92	0.0	93	0.0	94	2.0	95	0.0
96	0.0	97	0.0	98	0.0	99	0.0	100	0.0	101	4.0	102	1.0	103	5.0	104	1.0	105	3.0	106	0.0	107	0.0	108	0.0	109	0.0
110	0.0	111	0.0	112	1.0	113	1.0	114	2.0	115	2.0	116	1.0	117	13.0	118	2.0	119	2.0	120	0.0	121	0.0	122	0.0	123	0.0
124	0.0	125	0.0	126	0.0	127	0.0	128	0.0	129	0.0	130	0.0	131	8.0	132	98.0	133	27.0	134	3.0	135	1.0	136	1.0	137	1.0
138	0.0	139	0.0	140	0.0	141	0.0	142	0.0	143	0.0	144	0.0	145	2.0	146	32.0	147	100.0	148	12.0	149	1.0				

Figure 4. Print-Out Sheets of Instrument Parameters and Tabular Intensities (Actinidine).

The main program occupies 8186 cores of the computer. The plotting and lettering on the line drawing is accomplished by the two subroutines PLOT[5] and CHAR[6] furnished by the OSU engineering computing center. Since the PLOT subroutine takes an additional 2889 cores and the CHAR subroutine takes 4352 more cores of memory, while the IBM-1620 Fortran II-D system allows only 12500 cores for users' programs, it was necessary to cut the program into segments and run one segment each time through the computer. At present, the program has been cut into four portions and its core layout is shown in Table I.

The execution time is proportional to the total number of movements the pen has to make, but for an average spectrum, it is 4 to 5 min. The speed of drawing is limited by the speed of the plotting machine; however,

[5]Supplied by California Computer Products, Inc., Anaheim, California.

the time used by the computer itself is essentially negligible. Therefore, for on-line operation, it is not necessary to go to higher speed computers.

The present system has several advantages: a) the production of high-quality line drawings, b) print-out in tabular form of m/e values and relative intensities in a rectangular array, 10 most intense peaks, and metastable ions, c) the production of a permanent card deck for each compound. This system has the disadvantage that it has not been completely automated. We hope that a complete automatic data acquisition system will become available in the near future.

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TEN MOST INTENSE PEAKS OF SPECTRUM		METASTABLE IONS	
M/E	INT	M/E	INT
147	100.0	48.1	0.2
132	98.0	100.3	0.1
89	34.0	103.8	2.9
45	32.0	118.7	0.6
146	32.0		
133	27.0		
87	16.0		
73	14.0		
117	13.0		
148	12.0		

Figure 5. Print-Out Sheets of Ten Most Intense Peaks and Metastable Ions (Actinidine)

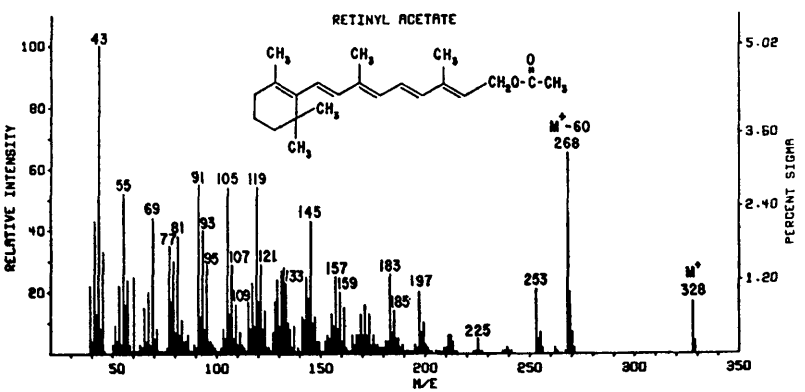

Figure 6. Mass Spectrum of Retinyl Acetate.

This spectrum was computer-plotted from tabular intensity data. A Cal Comp 565 Plotter driven by an IBM-1620 computer required about 3 min of plotting time and 4 min of computer time (for a Fortran II-D program).

TABLE 1. CORE STORAGE LAYOUT OF IBM-1620 COMPUTER FOR PROGRAM BARGRF AND SUB-ROUTINES.

	STARTING CORE ADDRESS	LENGTH OF PROGRAM
BARGRF	7500*	1612
PLOT	9112	2880
CHAR	11992	4352
FLIPER	16344	390
BARGF1	16736	2710
BARGF2	16736	1964
BARGF3	16736	1900
COMMON AREA	19769	230

*The core storage before 7500 is occupied by the supervisor, arithmetic, and input-output routines.

ACKNOWLEDGEMENTS

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