UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

A Computer Program Written in HPL for Acquisition and Reduction of Stable Isotope Data Using a Hewlett Packard 9825A Desktop Computer

By

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INTRODUCTION

Computer software utilizing the simple yet powerful interrupt features of the HP 9825A[1] desktop computer is designed to access and reduce analog/digital data (for light stable isotope analysis) from a conventional gas source ratio mass spectrometer. The instrumentation for which the software has been developed consists of the following, as illustrated in figure 1.

1. Nier-type 13 cm 60° sector gas source mass spectrometer, configured for double collection of the ion beams,
2. D.C. electrometer (EA) and vibrating reed electrometer amplifier (VRE) placed on the larger and smaller intensity signals respectively,
3. Matched Kelvin-Varley decade voltage dividers (10 kohm), and standard (10 mv) strip chart recorder for conventional graphic data collection (Nier, 1947; Nier and others, 1947; Deines, 1970; McKinney and others, 1950),
4. Nuclide Corp. integrating ratiometer IR-2A modified for HP 9825A control logic and with strobed BCD output formatted to HP 9825A interface requirements (Goodney and Kroopnick, 1978, discuss aspects of the integration method of analysis),
5. Hewlett Packard 9825A desktop computer, with 24 kbytes of R/W memory, Advanced Programming, String, and General/Extended I/O ROMS, further equipped with a BCD interface card and cable to the IR-2A, and a RS-232C interface to the DECwriter III printer.

The program can be adapted to numerous other possible instrument configurations. Though written in HPL for the HP 9825A, individuals familiar with either FORTRAN or BASIC will encounter no difficulty in translating the language to other real-time systems.

Somewhat greater measurement precision and no "operator error" in data reading and reduction are benefits of the digital method over the graphical analysis. Once the initial instrumental adjustments are made, no further operator participation is required to obtain a complete analysis. As a result, minimal operator skill and training are required for routine analysis. Instrumental, abundance, and working standard corrections (Deines, 1970) are stored in the program and must be modified in software as instrumental conditions change. A forced update in instrument calibration (every 400 hours of instrument time) is incorporated into the program and requires some time base, which is logged into the program at the start of each analysis. The program is capable of directly handling analyses of hydrogen, sulfur, and carbon isotopes, and of oxygen as (1) total oxygen (Taylor and Epstein, 1962; Clayton and Mayeda, 1963; and Northrop and Landis, 1981), (2) carbonate oxygen (McCrea, 1950), and (3) oxygen in water by CO_2 equilibration (Craig, 1957). A sample printout of hydrogen isotope analysis is given in figure 2.

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[1] Any use of brand or manufacturers' names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

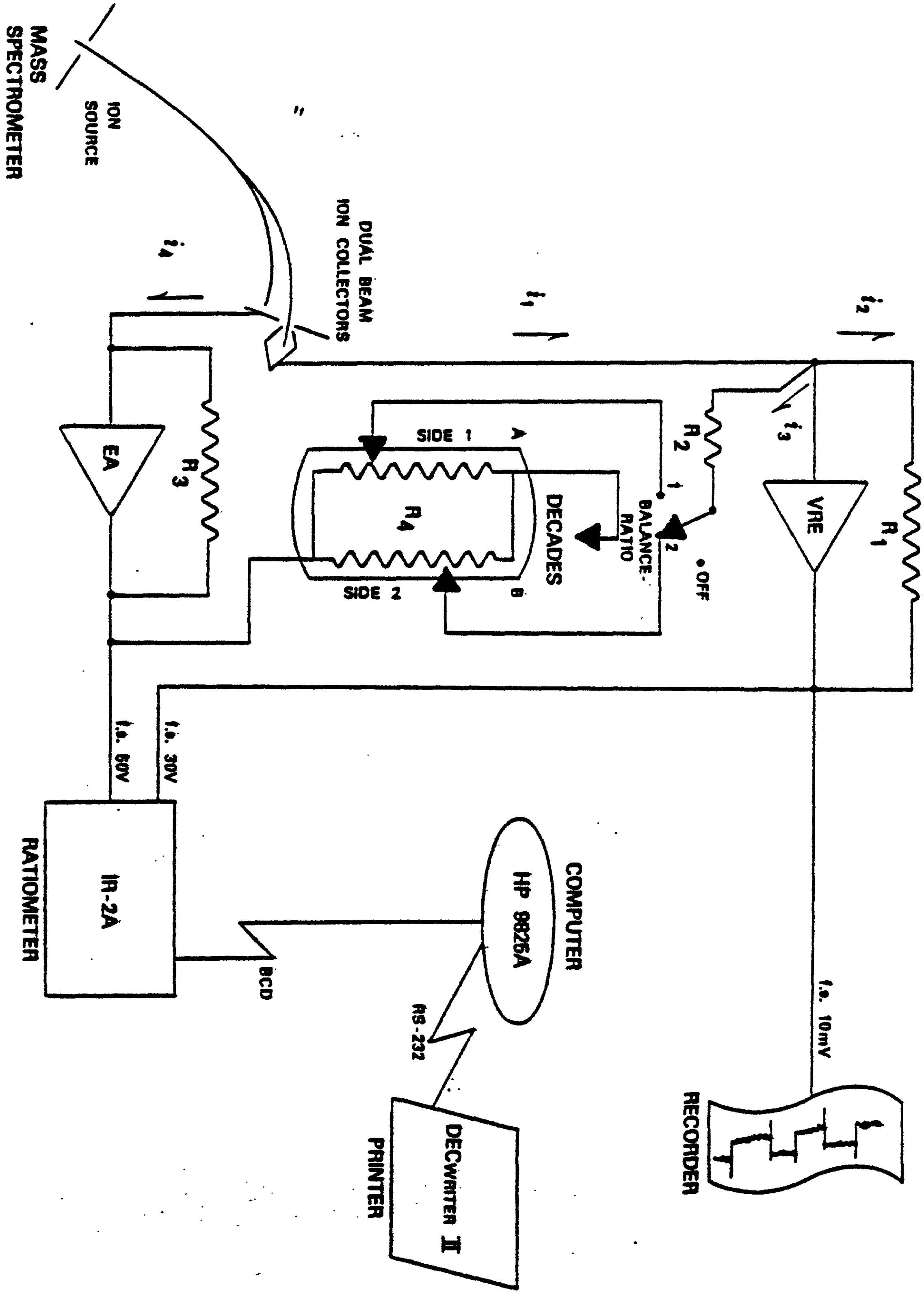
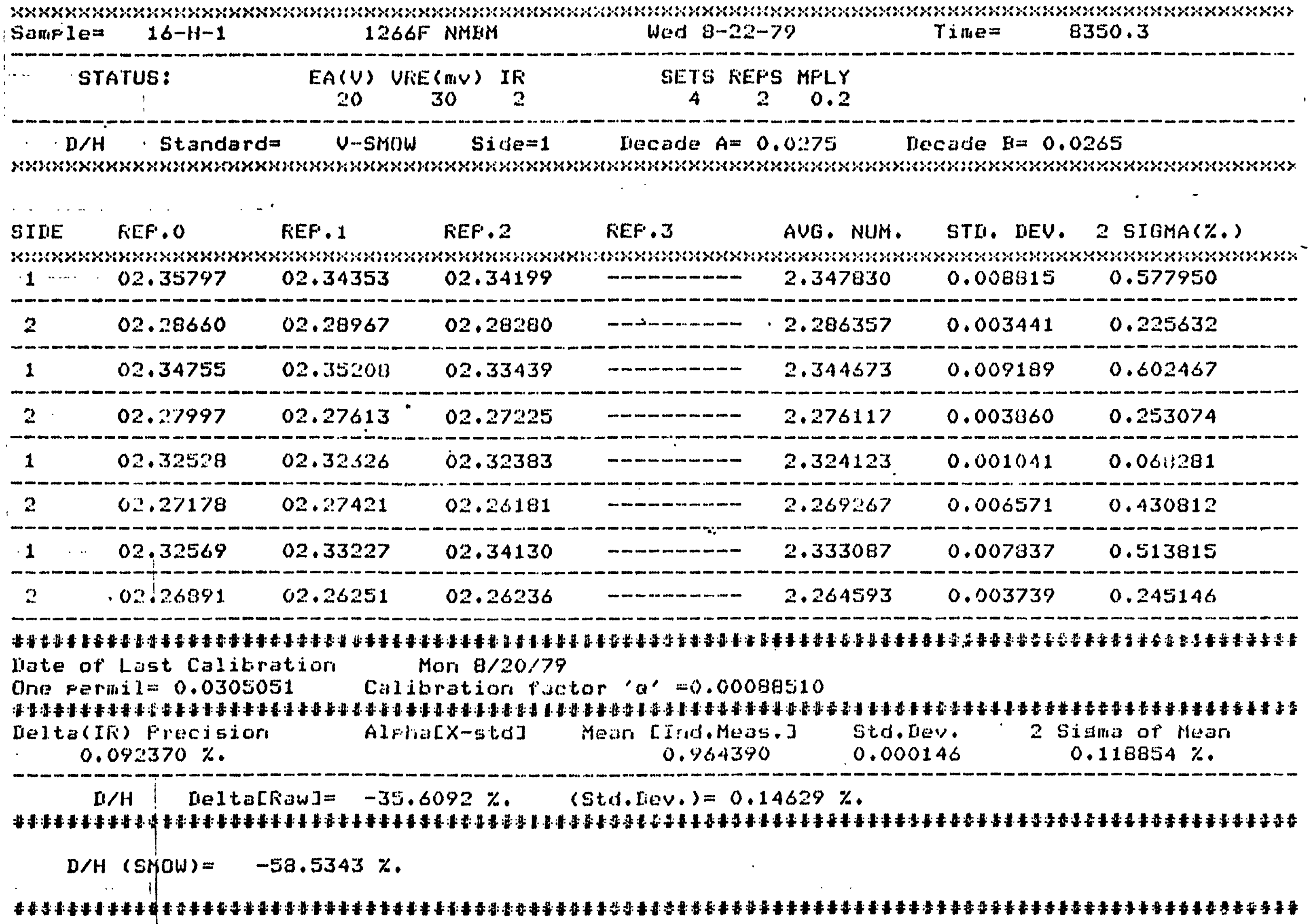


Figure 1.--Instrumentation Schematic



```
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX>
Sample=   16-H-1          1266F NMBM          Wed 8-22-79          Time=     8350.3
-----------------------------------------------------------------------------------------------------
    STATUS:              EA(V) VRE(mv) IR          SETS REPS MPLY
                          20     30    2             4    2   0.2
-----------------------------------------------------------------------------------------------------
    D/H    Standard=     V-SMOW    Side=1     Decade A= 0.0275     Decade B= 0.0265
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

SIDE    REF.0        REF.1        REF.2        REF.3          AVG. NUM.    STD. DEV.   2 SIGMA(%.)
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
 1      02.35797     02.34353     02.34199     ----------     2.347830     0.008815     0.577950
-----------------------------------------------------------------------------------------------------
 2      02.28660     02.28967     02.28280     ----------     2.286357     0.003441     0.225632
-----------------------------------------------------------------------------------------------------
 1      02.34755     02.35208     02.33439     ----------     2.344673     0.009189     0.602467
-----------------------------------------------------------------------------------------------------
 2      02.27997     02.27613     02.27225     ----------     2.276117     0.003860     0.253074
-----------------------------------------------------------------------------------------------------
 1      02.32528     02.32326     02.32383     ----------     2.324123     0.001041     0.060281
-----------------------------------------------------------------------------------------------------
 2      02.27178     02.27421     02.26181     ----------     2.269267     0.006571     0.430812
-----------------------------------------------------------------------------------------------------
 1      02.32569     02.33227     02.34130     ----------     2.333087     0.007837     0.513815
-----------------------------------------------------------------------------------------------------
 2      02.26891     02.26251     02.26236     ----------     2.264593     0.003739     0.245146
-----------------------------------------------------------------------------------------------------
#####################################################################################################
Date of Last Calibration        Mon 8/20/79
One permil= 0.0305051     Calibration factor 'a' =0.00088510
#####################################################################################################
Delta(IR) Precision       Alpha[X-std]      Mean [Ind.Meas.]     Std.Dev.      2 Sigma of Mean
    0.092370 %.                                 0.964390         0.000146          0.118854 %.
-----------------------------------------------------------------------------------------------------
      D/H     Delta[Raw]=   -35.6092 %.     (Std.Dev.)= 0.14629 %.
#####################################################################################################

    D/H (SMOW)=    -58.5343 %.

#####################################################################################################
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F I G U R E   2

Sample of Computer Output for a Typical Analysis

DATA ACQUISITION

Separate raw (full output voltage) signals are connected through buffered inputs (>10 megohm) to the modified Nuclide IR-2A integrating ratiometer from both the DC electrometer amplifier (EA) and the Cary 401M vibrating reed electrometer amplifier (VRE). Details of IR-2A circuit modifications should be requested from the author. Matched voltage-to-frequency converters, and decade counters are used to "integrate" the signals. The EA signal (collector signal of the larger ion beam) provides a time base, or denominator to the isotope ratio, by the volt-second setting on the IR-2A. For example, a 25 volt EA signal counted for 30 seconds would require a 750 volt-second setting. If the EA voltage dropped slightly, then the integration time would be lengthened to maintain a constant 750 volt-second. The VRE signal, or numerator while in the balance or ratio mode, is integrated over the interval determined by the constant EA denominator. The combined decade setting and numerator provide an analog measure of the ratio of ion currents. In standard fashion the sample and reference gas are alternately introduced into the mass spectrometer, repetitions of the integration are made, and the numerators collected. Numerator data and other operational information are read from the IR-2A to the HP 9825A using the BCD format in table 1. Standard permil notation is used in reporting the final analytical value,

$$\delta = 1000(R_{\text{sample}} - R_{\text{reference}})/R_{\text{reference}}$$

where R is the ion current (beam) ratio, and δ the permil value.

In place of the IR-2A integrator/ratiometer, stock analog-to-digital converters (A/D) could be substituted. The HP 9825A computer then reads the A/D output and provides the same integration or an averaged sample measurement. The computer would provide the time base for automatic switching of the inlet into the mass spectrometer of alternately gas #1 and gas #2. IR-2A provides this function in the present application.

DATA REDUCTION

The required programs are written in Hewlett Packard HPL language for use on a HP 9825A microcomputer. A flow chart and program listing are provided. But first it is important to completely understand the physical data measurements and their mathematical relations required to compute a meaningful stable isotope number. By making reference to the instrumentation configuration of figure 1, the conventional graphical means of analysis will be evaluated. This method will be conceptually adapted to digital procedures for unassisted computer control and analysis. Examination of this later digital method will also make use of numerical examples based upon CO_2.

Conventional Method

Data collection using separate signals from the E.A. (electrometer amplifier) representing the (44 + 45) m/e and from the V.R.E. (Cary 401M vibrating reed electrometer) representing the (46) m/e are handled in the ratio measurement circuit illustrated in figure 1. Note that for $\delta^{18}O$ analysis (CO_2) EA = 44 + 45 and VRE = 46; but for $\delta^{13}C$ analysis (CO_2) EA = 44 and VRE = 45. Also, for $\delta^{34}S$ analysis (SO_2) EA = 64 + 65 and VRE = 66; and for δD analysis (H_2) EA = 2 and VRE = 3.

Table 1.--BCD hexadecimal character position interface format to HP 9825A *

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
±	x	x	.	x	x	x	x	x	E	±	x	,	x	x	,

Position:

1) indicate inlet (gas) side: Side 1 = "-" Side 2 = "+"

2-9) numerator, with arbitrary decimal point in position 4

10) exponent "E" hardwired in interface

11) VRE signal polarity error: error indicated by "-"

12-13) not used

14) overload error = "8": indicates EA voltage is too high for the selected volt-second setting based upon VFC conversion rate

15) repetition number for the number of integrations per side, = 0,1,2,3

16) not used

*Four bit 8-4-2-1 BCD (binary coded decimal) characters, each bit TTL logic driven.

A typical $\delta^{18}O$ analysis (making reference to figure 1) involves obtaining

$$\frac{\phi R_3}{R_2} = \iota_1/\iota_4$$

for both sample gas and working lab reference standard gas, where ϕ = decade voltage divider setting (on R_4) for appropriate side, R_2 and R_3 are resistor values, and ι_1 and ι_4 are ion currents. The current ratio is an analog measure of the desired isotope ratio. Since R_3 and R_2 are fixed during an analysis, R_3/R_2 = constant = a. Therefore

$$\phi R_3/R_2 = a\phi \quad \text{and} \quad \iota_1/\iota_4 = a\phi$$

A raw, or uncorrected ratio, is proportional to the decade setting of the voltage divider $R_{raw} = \iota_1/\iota_4 \alpha \phi$
e.g., ϕ is proportional to the ratio of signals. To obtain a permil analysis one adjusts the decades for both sample and standard gas such as to "null" the output from the VRE. For example:

Sample DECADE A	= 0.2095	(Amphibole from LASL GT-2 Core)
Standard DECADE B	= 0.2127	(HIS Calcite Standard CO_2)

then:

$$\frac{R_{sample} - R_{standard}}{R_{standard}} * 10^3 = \delta^{18}O_{raw}$$

$$\frac{0.2095 - 0.2127}{0.2127} *1000 = -15.045 \text{ permil}$$

Note that in figure 1, ι_4 = the multiple collector (44 + 45) current to the EA, such that with a EA feedback resistor R_3 the EA voltage output becomes $E_\circ = -\iota_4 R_3$. $E_\circ$ is applied to the voltage decade divider R_4 (one for each gas side #1 and #2 labeled A and B). The divider output is

$$(\phi R_4)/R_4 * E_\circ = - (\phi R_4)/R_4 * \iota_4 R_3$$

where ϕ = the decade setting (e.g., 0.2095). If ι_1 is the small signal ion current arriving at the VRE and R_1 is the feedback resistor to the VRE, the feedback will hold the input to the VRE very near to ground potential such that ι_2 the feedback current is very small. Then the voltage across the ratio resistor R_2 is such that $E_2 = \iota_4 R_3(\phi R_4)/R_4$. At a "null output" of the VRE where a balance of ion currents is obtained by a unique decade setting $\phi_\circ$ ι_1 flows only through R_2.

That is:

$$\iota_1 = \iota_2 + \iota_3 \qquad (\iota_2 = 0 \text{ and } \iota_1 = \iota_3)$$

therefore:

$$\iota_3 R_2 = \iota_1 R_2 = \phi_\circ \iota_4 R_3$$

or

$$\iota_1 / \iota_4 = \phi R_3 / R_2$$

This is the important relationship between ion currents and physical settings on the instrument circuits. Any digital method will simply digitize the voltage output measurements for ratio calculations. This method is optimized if one makes $\phi > 0.1$; if $E_\circ = 50$ volts maximum, then R_2 or ι_1 is selected so that $\iota_1 R_2 < 50$ v.; $R_1 \leq R_2$; and noting that R_2 decreases the "loop gain" by a factor of $R_1/(R_1 + R_2)$.

In our example above, the raw or uncorrected analysis was -15.045 permil with respect to the machine standard. However, for this analysis the precise "null" position was not obtained by the use of the indicated decade settings (e.g., resolution of 4 decimal places on the decade boxes is not sufficient). Therefore, a residual current is left at the input to the VRE which produces a voltage at the VRE output. This signal is put on the strip chart recorder and a trace made of sample, then of standard, then of sample, etc., for 6 to 10 repetitions. The resulting recorder trace is illustrated in figure 3. The difference in output between sample (1) and standard (2) can be translated into additional precision of the analysis. First, the sensitivity of the measurement system must be determined. That is, the permil offset per chart division on the recorder paper must be known. For this analysis one chart division is equal to 0.0825 permil. The offset of the standard and sample in the actual analysis is $\Delta = -1.2$ chart divisions. Note that the sample is a smaller signal than the standard, giving a negative offset. Therefore, the actual offset is (-1.2) * (0.0825) = -0.099 permil, and the more precise raw machine analysis is -15.045 + (-0.099) = -15.144 permil. Note that a sensitivity is determined by simply producing an artificial offset on the strip chart recorder using the same gas and changing the decade setting back and forth to two values to generate "X" permil apparent offset of "Y" chart divisions. This measurement reduces to "S" permil/chart division and should be determined routinely during operation of the mass spectrometer.

Circuit Analysis.--During the isotope analysis for the above example the EA = 25 volts, the VRE = 30 millivolts full scale, $R_2 = 2 \times 10^{11}$ ohm and $R_3 = 1 \times 10^{10}$ ohm. R_1 (feedback resistor on VRE) = 2×10^{11} ohm. By changing any of the above parameters, a new sensitivity determination is required. Analysis of circuit performance is as follows:

$$E_\circ = 25 \text{ v.}$$

$$E_\circ / R_3 = \iota_4 = 25 \text{ v}/(1 \times 10^{10}) = 2.5 \times 10^{-9} \text{ amp.}$$

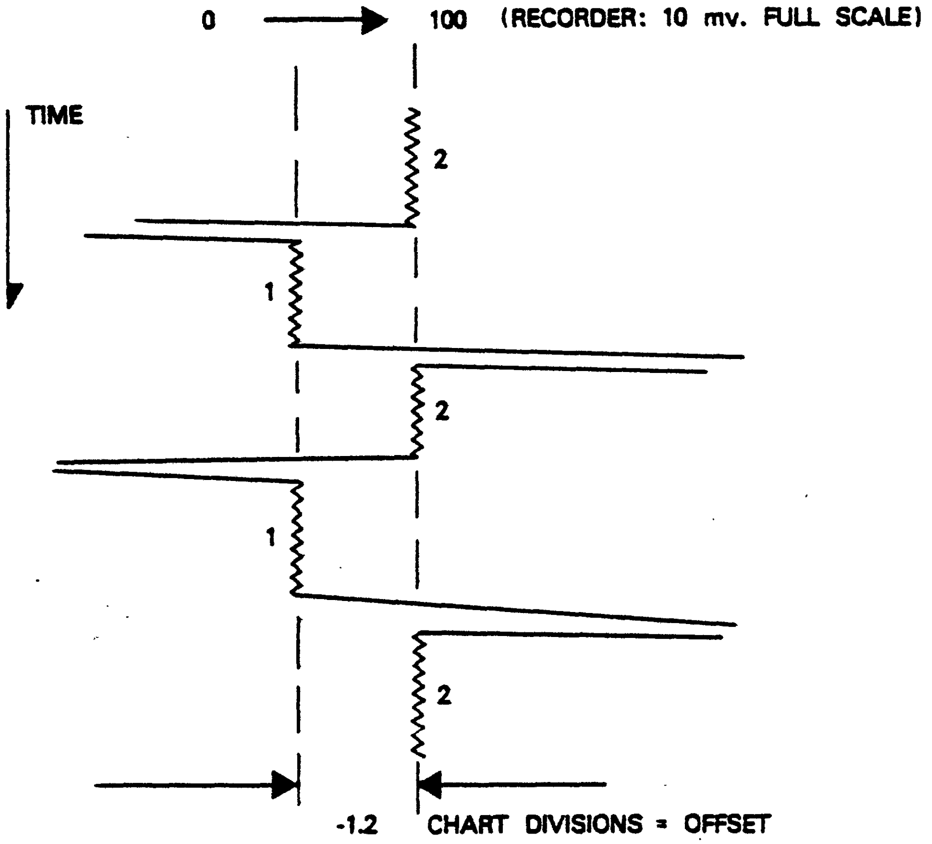

Figure 3.—Strip Chart Trace of Residual VRE Output

The output of R_4 to R_2 is

$$\Phi E_\circ = 0.2127 * 25 = 5.318 \text{ v.}$$

and $\iota_3 \simeq 2.659 \times 10^{-11}$ amp.

if VRE = 15 mv (on 30 mv f.s.)

the VRE is measuring a new current of:

$$E_{VRE}/R_1 = 0.015/(2.0 \times 10^{11}) = 7.5 \times 10^{-14} \text{ amps.}$$

and $\iota_1 = \iota_4 \, \Phi \, R_3/R_2 + E_{VRE}/R_1 = 2.66 \times 10^{-11}$ amps.

or $\iota_1 = \iota_3 + \iota_2 = 2.66 \times 10^{-11}$ amps.

Therefore: $\iota_1/\iota_4 = 0.010685 = \phi \, R_3/R_2 + R_3/R_1(E_{VRE}/E_\circ)$.

Digital Integration Method

By use of the integrating ratio digital voltmeter (IR-2A) and HP 9825A computer, a complete raw permil value can be determined without operator participation. Slightly greater precision, no operator data reading and interpretation error, and substantial convenience are the obvious advantages. Calculations using digital methods without computer assistance, however, are very long and tedious.

A "ratio" is obtained from the same EA and VRE signals discussed above. Two voltage-to-frequency converters and separate decade counters are used. The EA 25 volt signal is used internally to provide a time base for integration of the VRE "residual" signal present in the balance or null mode. The EA signal of 25 volts times the length of integration in seconds is set on the volt-second dial of the IR-2A; e.g., 25 v. times 30 sec. integration time is 750 volt-second setting on the dial. During this period the VRE 0-30 volt (on 30 mv range) signal is integrated and presented as a seven-digit number at the output. Since the EA signal level is determining the integration time for the VRE signal, the EA (multiple collector 44 + 45) is considered the "denominator" and the 7-digit VRE output (46) the "numerator." For a constant volt-second setting, the numerator is actually a ratio. The following discussion is an example of data obtained for the same analysis of the sample discussed above. Actually, both graphic and digital methods of data collection are conducted simultaneously. Agreement of results confirms correct system operation.

Calibration.--Before an analysis can be performed, the "numerator" value must be calibrated so that an integration number difference between sample and standard gas can be related to a permil difference. This method is accomplished in a fashion analogous to that used to calibrate the recorder offset. In fact, both calibration sensitivities are determined concurrently by operating both the recorder and the integrator. Either sample or standard gas is analyzed alone while the instrument is in ratio or balance mode. A decade position is chosen to put the VRE output at mid-scale (e.g., the recorder trace at approximate center). Next, a second position is chosen to produce, with the same gas, an offset of 2-4 times that normally experienced during an analysis. Repeated integration or strip-chart readings are made at both these decade positions "1" and "2," producing 3-6 sets of integrations for both that at decade position "1" and at decade position "2." As an example, the following data were generated in an actual run:

Calibration Data: performed on same gas

Decade position "1" = 0.2142

Decade position "2" = 0.2159

0: 1st integration

1: 2nd integration

X: Average of integrations (max = 4, or 0,1,2,3)

σ: Standard deviation of number of integrations

Position "1"	Position "2"
0: 25.12932	
1: 25.00639	
X: 25.06786	
σ: 0.08692	

Position "1"	Position "2"
	0: 4.12798
	1: 4.11717
	X: 4.12258
	σ: 0.00764
0: 25.16175	
1: 25.32630	
X: 25.24403	
σ: 0.11635	
	0: 4.17171
	1: 4.12549
	X: 4.14860
	σ: 0.03268
0: 24.97112	
1: 25.13683	
X: 25.05398	
σ: 0.11717	
	0: 4.13507
	1: 4.17986
	X: 4.15747
	σ: 0.03167

Summary:

Position	Average X	Difference $\|\Delta\|$
1	25.06786	
		20.94528
2	4.12258	
		21.12145
1	25.24403	
		21.09543
2	4.14860	
		20.90538
1	25.05398	
		20.89651
2	4.15747	
		104.96405

Average Numerator Difference = 20.99281

Decade Permil Offset: = 7.905 permil

$$\frac{\text{Decade Difference}}{\text{Decade Average}} * 1000 = \frac{0.2159-0.2142}{0.5(0.2159-0.2142)} *10^3$$

Define Sensitivity as the integrator (numerator) digits per permil

Sensitivity = F = 20.99281 / 7.905 = 2.6556 digits/permil

Define Calibration Factor as $\partial \text{Decade}/\partial|\Delta|$

$$q = \Delta \text{ Decade} / (\text{Average } |\Delta|) = \frac{0.0017}{20.99281} = 0.00008098$$

For the Amphibole sample of LASL GT-2 core

$F = 2.6565$ $\quad$ $q = 0.00008018$

These numbers must be entered into the program on a regular basis, and must be updated every 400 hours or as optionally requested at the beginning of program execution.

Sample Analysis.--With the instrument calibrated, the sample can be analyzed. Because of the linear relationships in the circuit design, the following equation applies:

$$R = p(D + qI)$$

where: R = actual ratio of ions ι_1/ι_4

p = measured, current ratio * R_3/R_1

D = decade setting

q = correction factor or "calibration factor"

I = "numerator" (the integrated reading)

and for small changes

$R/p = D + qI$ becomes $\Delta D + q\,\Delta I = 0$

$$q = \frac{-\Delta D}{\Delta I}$$ (Note that q is always positive)

In order to find the raw delta ($\delta^{18}O_{raw}$) between the sample and the standard or reference gas

$$\delta^{18}O_{raw} = 1000\,(R_1 - R_2)/R_2$$
$$= \frac{D_1 - D_2 + q\,(\bar{I}_1 - \bar{I}_2}{D_2 + q\,\bar{I}_2}$$

where D_2 and D_1 and $\bar{I}_2$ and $\bar{I}_1$ refer to decade settings and average integrator readings for standard and sample respectively. Now consider an actual sample analysis.

Sample: Amphibole, LASL GT-2 core.

Decade A (Side 1) sample = 0.2095
Decade B (Side 2) standard = 0.2127

Sample Side 1	Standard Side 2
0: 12.82092	
1: 13.36933	
2: 13.21047	0: 13.23754
	1: 13.40822
X: 13.13357	2: 13.92647
σ: 0.28218	
	X: 13.52408
	σ: 0.35878

0: 13.40817
1: 12.98327
2: 13.23881

X: 13.21008
σ: 0.21390

0: 13.24925
1: 12.75989
2: 12.30721

X: 12.77212
σ: 0.47114

0: 13.30000
1: 13.59868
2: 13.67942

X: 13.52603
σ: 0.19987

0: 13.00692
1: 13.50095
2: 13.59006

X: 13.36598
σ: 0.31413

Side	- Ratio	$\bar{X}$ (avg. Num.)	Corrected # Decade No.	R(sample) * R(standard)	$\delta^{18}O_{raw}$ †
1	R1	13.13357	0.2105530		
2	R2	13.52408	0.2137844	0.9848993	-15.101
1	R3	13.21008	0.2105592	0.9849135	-15.086
2	R4	13.52603	0.2137845	0.9848312	-15.169
1	R5	13.77212	0.2105241	0.9847786	-15.221
2	R6	13.36598	0.2137717		
			Average:	0.9848557	-15.144
			σ:	0.0000627	0.063

Define Corrected Decade No. as $D_c = D + q\,\bar{I}$

* To take account of drift in trace of numerator the following procedure is used:

(a) $\frac{R1 + R3}{R2} = R_A;\ R_A/R2 = \alpha_{x\text{-std.}}$

(b) $\frac{R2 + R4}{R3} = R_A;\ R_A/R3 = \alpha_{std.\text{-}x}$ or $1/\alpha = \alpha_{x\text{-std.}}$

(c) $\frac{R3 + R5}{R4} = R_A;\ R_A/R4 = \alpha_{x\text{-std.}}$

(d) etc......

keeping in mind that $\frac{R(\text{sample})}{R(\text{standard})} = \frac{\bar{D}(\text{corrected})}{\bar{D}_2(\text{corrected})} = \alpha_{x\text{-std.}}$

†$(\alpha - 1) * 10^3 = \delta^{18}O_{raw}$ permil

Note that $\delta^{18}O_{raw}$ = -15.144 permil is the same value as that obtained by the graphical method described above.

Analysis Statistics.--Several statistical parameters are calculated as a means of judging the "quality" of a particular analysis. For a given instrumental configuration an operator with some experience is able to recognize the condition of the machine performance and either accept or reject a particular analysis. The following are routinely computed during and at the end of each analysis: (a) the mean of the fractionation factor for the sample, α; (b) the standard deviation of α; (c) coefficient of variance; (d) the precision of the measurement; and (e) the internal precision at 95 percent confidence. These functions are defined below as they are calculated in the programs.

Mean: $\bar{\alpha} = \bar{X} = \frac{\Sigma X}{n} = 0.9848557$

$\alpha(X)$	$X - \bar{X}$	$(X - \bar{X})^2$
0.9848993	0.0000436	1.90096×10^{-9}
0.9849135	0.0000578	3.34084×10^{-9}
0.9848312	0.0000245	6.00250×10^{-9}
0.9847786	0.0000771	5.94441×10^{-9}
		$\Sigma\ 11.78646 \times 10^{-9}$

Standard Deviation:

$$\sigma_{(\alpha)} = [\Sigma(X - \bar{X})^2/(n-1)]^{1/2} = [11.78646 \times 10^{-9}/3]^{1/2}$$

$$= \pm\ 0.00006268$$

Coefficient of Variance: $\frac{\sigma}{\bar{X}} * 100 = 0.0063644\ \%$

Internal Precision of Mean [At Approximately 90 Percent Confidence]:

$$\frac{2\sigma}{\bar{X}\ n} * 100 = \text{I.P.} = \pm\ 0.0063644\%$$

note: $\frac{2\sigma_x}{n} = 2\sigma_{mean}$

by replacing 2 above with student's-t precise confidence limits can be maintained.

Internal Precision of Measurement (Δ Integrator):

$$\sigma = \frac{\sqrt{\Sigma(X - \bar{X})^2/(n - 1)}}{\sqrt{n}}$$

Side	Average	Difference(X)	$X-\bar{X}$	$(X - \bar{X})^2$
1	13.13357			
2	13.52408	0.39051	0.083136	0.006912
1	13.21008	0.31400	0.159646	0.025487
2	13.52603	0.31595	0.157696	0.024868
1	12.77212	0.75391	0.280264	0.078548
2	13.36598	0.59386	0.120214	0.014451

$\bar{X} = 0.473646$ $\Sigma = 0.150266$

$$= [0.150266/4]^{1/2}/[5]^{1/2} = \pm 0.08668$$

Precision (permil):

σ/F permil = 0.08668/2.6565 = ± 0.03263 permil

Statistical Summary of Analysis:

$\delta^{18}O_{raw}$ = -15.144 permil ± 0.06268 permil

Precision: = ± 0.03263 permil ΔIR

α:

mean = 0.9848557

$\sigma = \pm 0.00006268$

Relative Standard Deviation = ± 0.0063644%

Internal Precision [90 Percent Confidence] = ± 0.00636%

Analytical Corrections to Raw Value

To obtain a final result from the raw permil value, several corrections must be applied. These considerations are amply discussed in the literature and will not be evaluated here. A brief summary is provided to indicate that the program does make these corrections in order to calculate a final result. The operator must input these numbers, and in the case of instrumental corrections, periodically update the correction entries to the program. The corrections are as follows:

I. Instrumental (Frank, 1978; Deines, 1970)
  A. Valve mixing
  B. Decade match (zero enrichment)-capillary leak
  C. Background
  D. Tail (abundance sensitivity)

II. Abundance Correction (Craig, 1957; Hulston, 1964)

III. Standard Correction to SMOW, PDB, CDT, etc. (Craig, 1957, 1961; Gonfiantini, 1977)

The general form of application of these corrections is

$$(\text{Abundance}) * \Sigma\ (\text{Instrumental}) * \delta_{raw} = \delta_{machine} = \delta_{x\text{-}WS}$$

and $\delta_{x\text{-}RS} = \delta_{x\text{-}WS} + \delta_{WS\text{-}RS} + 10^{-3} * \delta_{x\text{-}WS} * \delta_{WS\text{-}RS}$

where
x = sample
RS = reference (reporting) standard
WS = working (machine) standard

Instrumental corrections are of two basic categories. The first set of corrections results from the use of pairs of instrumental components that do not perform identically for both sides of the inlet for standard and sample gas. These include valve mixing, decade pairs, capillary pair leaks, and side #1 and side #2 inlet vacuum chambers. The second set of instrumental corrections is the result of extraneous ion currents in the source, collector, and flight tube of the mass spectrometer. These factors include the major peak tail dispersion and the background corrections.

Abundance corrections are constant factors applied to the raw analysis because the measurement of ion currents is not directly in a form related to the reported analysis of (minor isotope)/(major isotope). That is, the desired $^{18}O/^{16}O$ ratio is actually measured as m/e of 46/(44 + 45). This ratio is corrected with the abundance correction which is based upon natural abundance data of the isotopes in question. A standard correction is required whenever the machine standard is different from that of the international reporting standard.

The insertion points in the program for the various types of analysis are clearly labeled and can be located from the program listing. The operator must modify the various correction parameters to reflect the instrumental conditions.

COMPUTER PROGRAM

The program, written in HPL language exists on tape in two versions to enable the output of data to be directed either to the internal 16 character thermal printer, or to any RS-232C ASCII printer. The tape structure, which allows for auto loading of appropriate files and tape maintenance, is described in table 2. The complete listing of all file contents is given in table 3. The programs implement the data acquisition and reduction described in the previous sections. A flow chart (fig. 4) illustrates the main segments of the program as well as identifies and defines important variable names.

The program consists of five functionally and conceptually distinct parts which physically are nearly separate. They are as follows: (1) Set up of control and sample input; (2) Data collection; (3) Data reduction and statistical evaluation; (4) Corrections to data; and (5) Calibration. For computers having less memory, this program can be divided into separate files and chained together for execution. In this manner the program is executed easily in minimum HP 9825A R/W memory. Any desired modifications should be readily accomplished using the flow chart as a reference.

Table 2

Program Tape Structure and Function

File 0:
- * Auto load program and execute with power up of computer.
- * Increment counter A = B; if A > 20, reset A = 1
- * Load A into File 1
- * If B > 20, go to end of File 10, rewind-erase tape to end, and return. This eliminates slack tape and possible damage.
- * Load File 2: Special Function Keys definitions
- * Choose Printer for Output:

    11 = External ASCII printer on RS-232C
    Load File 5

    16 = Internal 16 Character Printer of HP 9825A
    Load File 3

File 1: Tape Wind Counter A

File 2: Special Function Keys

File 3: Program with I/O Support for HP 9825A Printer

File 4: Calibration Data Arrays:

K[54,2] = Calibration Parameters
K(*,1] = F   K[*,2] = q
K$[54,12] = Date of Calibration
T$[54,8] = Machine Time of Calibration

Data are in 54 element linearized matrix

VRE Range	10 mv			30 mv			100 mv		
Input Resistor	1	2	3	1	2	3	1	2	3
$\delta^{34}S$	1	2	3	4	5	6	7	8	9
$\delta^{13}C$	10	11	12	13	14	15	16	17	18
δD	19	20	21	22	23	24	25	26	27
$\delta^{18}O$-T	28	29	30	31	32	33	34	35	36
$\delta^{18}O$-C	37	38	39	40	41	42	43	44	45
$\delta^{18}O$-W	46	47	48	49	50	51	52	53	54

File 5: Program with I/O Support to RS-232C External ASCII Printer

Table 3.--Tape File Structure and Program Listings

File 0:

Autoload and tape wind: select printer internal [16] or external [11]

```
0: ldf 1,A
1: A+1→A→B
2: if A>20;1→A
3: rcf 1,A
4: if B>20;fdf 10;ert 10
5: ldk 2
6: ent "Which printer for output?",H
7: if H=16;ldf 3
8: if H=11;ldf 5
*8715
```

File 1:

Tape wind counter → A

File 2:

Special Function Keys

```
f0:  /S(34)
f1:  /C(13)
f2:  /D/H
f3:  /O(18)-T
f4:  /O(18)-C
f5:  /O(18)-W
f6:  /yes
f7:  /no
f8:  *→r36;1.8*r36+32→r37;dsp'Degree',char(31),r36,'C=',r37,'F'
f9:  *→r36;(r36-32)/1.8→r37;dsp'Degree',char(31),r36,'F=',r37,'C'
f10:  *→r36;fxdr36
f11:  *cont'START'
f12:  *cont'CONST'
f13:  *cont'TAB'
f14:  *(r31*1e6/(1e3ln((r34+1e3)/(r35+1e3))-r32))↑.5-273.16→r33;
      dsp'Temp=',r33
f15:  *(r35+1e3)exp(r31*1e3/(r33+273.16)↑2+r32*1e-3)-1e3→r34;
      dsp'B=',r35,'%.'
f16:  *(r34+1e3)/exp(r31*1e3/(r33+273.16)↑2+r32*1e-3)-1e3→r35;
      dsp'B=',r35,'%.'
f17:  *(r34+1e3)/(r35+1e3)→r36;dspchar(4),'=',r36
f18:  *1e3ln((r34+1e3)/(r35+1e3))→r36;dsp'1000ln',char(4),'=',r36
f19:  *→r33;1/(r33+273.16)↑2*1e6→r36;dsp'1/T',char(29),'x10↑6=',r36
f20:  *→r33;r33/2,54→r36;dspr33,'cm=',r36,'in.'
f21:  *→r33;2,54*r33→r36;dspr33,'in.=',r36,'cm.'
f22:  *→r36;fltr36
f23:  *cont'ENT'
```

Table 3.--Tape File Structure and Program Listings

File 3:

Mass Spectrometer Program with Output to Internal Program [16]

```
0: "W":dim H[40],X[20],M[40],D[40],B$[8],C$[8],D$[16],F,Q
1: dim A$[3],S[0:81],R[80],N[80],S$[16],C[40],E$[8],F$[1],R$[3]
2: dim J$[16],H$[3],E[20],G$[20],U[2],K[54,2],K$[54,12],T$[54,8],I$[32]
3: dim L$[3],A[80],P$[8],Z[1],Z$[5],V[10]
4: ldf 4,K[*],K$,T$
5: buf "Dump",I$,1
6: 87621→U[1]→U[2]
7: dsp "MASS SPEC DATA REDUCTION PROGRAM";stp
8: ent "Day-Date(eg=Mon_12/27/77)",D$
9: ent "Standard Used:[8 characters]",B$
10: ent "On which side is standard gas ?",E;jmp 4
11: "START":dsp "New Sample";spc 4;1→M
12: beep;wait 250;jmp (M+1→M)>50
13: 1→M;stp
14: ent "Lab Number ?",S$,"Sample Name",J$
15: jmp 2
16: spc 2;stp
17: char(18)→F$
18: ent "Which Stable Isotope Analysis:",C$
19: F$&C$→C$
20: ent "EA=",r4,"VRE=",r5,"IR=",r6
21: ent "Setting:Decade A ?",A,"Setting:Decade B ?",B
22: jmp 2
23: spc 2
24: ent "No. Data Sets Per Side[min=3]",r40,"Repetition No.",R
25: ent "[IR] Multiplier",Z[1];2r40*(R+1)→I
26: if I>80;dsp "Array Overload";wait 5000;jmp -2
27: ent "Machine Time?",E$
28: "ALL":fmt 1,16"x";fmt 2,c7,c9,/,c16;fmt 3,16"-";fmt 4,c12;fmt 5,c5,3x,c8
29: fmt 6,5x,"STATUS",5x,/,"EA(v) VRE(mv) IR",/,2x,f2.0,4x,f3.0,4x,f1.0
30: fmt 7,4x,c8,4x;fmt 8,"Std=",c8,":S=",f1.0
31: fmt 9,"Calibration Run"
32: wrt 16.1;wrt 16.2,"Sample=",S$,J$;wrt 16.3
33: wrt 16.4,D$;wrt 16.5,"Time=",E$;wrt 16.3
34: wrt 16.6,r4,r5,r6;wrt 16.3;fmt 6,"Sets  Reps  Mply";wrt 16.6
35: fmt 6,1x,f2.0,5x,f1.0,4x,f3.1;wrt 16.6,r40,R,Z[1];wrt 16.3
36: wrt 16.7,C$;wrt 16.8,B$,E
37: fmt 2,"Decade A=",f7.4,/,"Decade B=",f7.4
38: wrt 16.2,A,B;wrt 16.1
39: ent "Any Corrections ?",L$;if L$="yes";spc 4;gto "START"
40: if C$=F$&"S(34)";0→r7
41: if C$=F$&"C(13)";9→r7
42: if C$=F$&"D";18→r7
43: if C$=F$&"O(18)-T";27→r7→r47
44: if C$=F$&"O(18)-C";36→r47;27→r7
45: if C$=F$&"O(18)-W";45→r47;27→r7
46: if r5=10;r7+r6→r8
47: if r5=30;r7+r6+3→r8
48: if r5=100;r7+r6+6→r8
49: Z[1]*K[r8,1]→F;1/Z[1]*K[r8,2]→Q
50: val(E$)-val(T$[r8])→r38
*17892
```

Table 3.--Tape File Structure and Program Listings

```
51: if r38>400;"yes"→A$;dsp "Calibration Update Required";wait 5000;jmp 2
52: ent "Is this calibration ?",A$
53: if A$="yes";wrt 16.9;wrt 16.1;jmp 2
54: spc 2;jmp 2
55: dsp "[IR] Multiplier to 1X Position";stp
56: if A$#"yes";jmp 7
57: ent "Decade A=",r45,"Decade B=",r46
58: fmt 2,"Decade A=",f7.4,/,"Decade B=",f7.4
59: ent "No.Data Sets Per Side[min=3]",r40,"Repetition No.",R
60: ent "[IR] Multiplier",Z[1];2r40*(R+1)→I
61: if I>80;dsp "Array Overload";wait 5000;jmp -2
62: wrt 16.2,r45,r46;wrt 16.1
63: fmt 4,"Side",1x,"Rep",3x,"Num",2x,;wrt 16.4;wrt 16.1
64: fmt 2,f3.0,f4.0,1x,c8
65: fmt 6,3x,f4.0,1x,c8;fmt 7,c8,f8.5;fmt 8,"Std.Dev=",f8.5
66: fmt 9,1x,c2,b,c2,f6.4,c4
67: "ENT":dsp "Verify Mass Spec Status";wait 5000
68: dsp "When Ready, Push Start-Reset[IR]"
69: wtc 3,32
70: "REC":1→K;0→T;0→r1;1→S[0]
71: for J=1 to I+1
72: if J=I+1;jmp 10
73: buf "Dump";if J=2;dsp ""
74: tfr 3,"Dump"
75: jmp rds("Dump")=16
76: red "Dump",G$
77: 2→S[J];if G$[1,1]="-";1→S[J]
78: val(G$[2,9])→N[J];G$[2,9]→P$
79: val(G$[15,15])→R[J]
80: if val(G$[14,14])=8;0→N[J];"Overload"→P$
81: if G$[11,11]="+";0→N[J];"NegError"→P$
82: gto "AVG";if S[J-1]=S[J];gto "RET"
83: "RET":if J=I+1;gto "CONT"
84: gto "TWO";if R[J]=0;gto "ONE"
85: "ONE":wrt 16.2,S[J],R[J],P$;jmp 2
86: "TWO":wrt 16.6,R[J],P$
87: if A$#"yes";jmp 5
88: if R#R[J];jmp 4
89: 1→M
90: beep;wait 50;jmp (M+1→M)>20
91: 1→M
92: N[J]+T→T
93: if N[J]>0;r1+1→r1
94: gto "CONT"
95: "AVG":if r1=0;prt "*****ABORT******";gto "ENT"
96: T/r1→r2;0→N
97: if R=0;gto 108
98: wrt 16.7,"Avg.Num=",r2
99: for V=1 to R+1
100: if N[J-V]=0;jmp 2
*27706
```

Table 3.--Tape File Structure and Program Listings

```
101: (N[J-V]-r2)↑2+N→N
102: next V
103: √(N/(r1-1))→N;wrt 16.8,N
104: if A$="yes";jmp 2
105: 2N/F→N;wrt 16.9,"(2",9,"= ",N," %.)"
106: r2→C[K];S[J-1]→A[K];K+1→K
107: wrt 16.3;0→T;0→r1;gto "RET"
108: "CONT":next J
109: if A$="yes";gto "CAL"
110: if E=1;A→r1;B→r2;jmp 2
111: if E=2;B→r1;A→r2
112: fmt 1,c11,5x,/,f16.4;fmt 4,16"#";fmt 2,c12
113: wrt 16.4;wrt 16.2,K$[r8];wrt 16.3;wrt 16.1,"One permil=",F
114: fmt 1,c11,5x,/,c12,4x,/,f16.8
115: wrt 16.1,"Calibration","Factor 'q' =",Q
116: wrt 16.4
117: 0→M→N
118: for J=1 to K-2
119: abs(C[J]-C[J+1])→M[J];M+M[J]→M
120: next J
121: M/(K-2)→M
122: for J=1 to K-2
123: N+(M[J]-M)↑2→N
124: next J
125: √(N/(K-3))/√(K-2)/F→P
126: for J=1 to K-1
127: if A[J]=1;A+Q*C[J]→H[J];jmp 2
128: if A[J]=2;B+Q*C[J]→H[J]
129: next J
130: sfg 4
131: if E=2;cfg 4
132: 1→L;E→r10;0→D
133: for J=1 to K-3
134: Q*((C[J]+C[J+2])/2-C[J+1])→r9
135: if flg4;-r9→r9
136: cmf 4
137: (r2-r1+r9)*1000/H[r10]→D[L]
138: if J=1;r10+2→r10;0→I
139: if I=2;r10+2→r10;0→I
140: I+1→I
141: D[L]+D→D;L+1→L
142: next J
143: cfg 4;D/(L-1)→U
144: 0→S
145: for J=1 to L-1
146: (D[J]-U)↑2+S→S;next J
147: √(S/(L-2))→S
148: sfg 4
149: if E=2;cfg 4
150: 1→I;0→X
*3619
```

Table 3.--Tape File Structure and Program Listings

```
151: for J=1 to K-3
152: .5(H[J]+H[J+2])/H[J+1]→X[J]
153: if flg4;1/X[I]→X[I]
154: cmf 4
155: X+X[I]→X;I+1→I
156: next J
157: X/(I-1)→X;0→V
158: for J=1 to I-1
159: (X[J]-X)↑2+V→V
160: next J
161: r(V/(I-2))→Z
162: (X-1+2Z/r(I-1)-(X-1))1000→T
163: fmt 1,16"#";fmt 2,16"-"
164: fmt 3,c11,b,c3,x,/,3x,f8.6,x,c2
165: fmt 4,4x,b,"(X-std)",4x,/,c16,/,c5,b,c1,f9.6
166: fmt 5,c9,b,c1,5x,/,3x,f11.9,2x
167: fmt 6,c1,b,x,c7,x,b,4x,/,c16,/,3x,f11.9,c2
168: fmt 7,4x,c8,4x
169: fmt 8,b,c4,x,f8.3,c2
170: fmt 9,3x,b,c,f9.7,c2
171: wrt 16.3,"Precision (",8,"IR)",P,"%."
172: wrt 16.2;wrt 16.4,4,"Individual Meas.","Mean ",2,"=",X
173: wrt 16.5,"Std.Dev. ",9,"=",Z
174: wrt 16.6,"2",9,"of Mean",4,"@ 95% Confidence",T,"%."
175: wrt 16.1
176: wrt 16.7,C$
177: wrt 16.8,18,"[R]=",U,"%."
178: wrt 16.9,9,"=",S,"%."
179: wrt 16.1;gto "E"
180: "CAL":0→L
181: r45→r1;r46→r2
182: for J=1 to K-2
183: abs(C[J]-C[J+1])+L→L
184: next J
185: L/(K-2)→r48;r2-r1→r49;(r1+r2)/2→r50
186: 1000r49/r50→r51;abs(r48/r51)→F;abs(r49/r48)→Q
187: fmt 1,c11,5x,/,f16.4;fmt 4,16"#"
188: wrt 16.4;wrt 16.1,"One permil=",F
189: fmt 1,c11,5x,/,c12,4x,/,f16.8
190: wrt 16.1,"Calibration","Factor 'q' =",Q;wrt 16.4
191: ent "Save Cal ?",R$;if R$#"yes";jmp 3
192: F→K[r8,1];Q→K[r8,2];D$→K$[r8];E$→T$[r8]
193: rcf 4,K[*],K$,T$
194: ent "Do you wish analysis ?",R$
195: gto "END";if R$="yes";"   "→A$;gto 24
196: "E":
197: "Calibration Routines":
198: fmt 1,16"#"
199: fmt 2,/,c8,x,c7,/,2x,f9.4,x,c2,2x,/
200: "INSTRUMENTAL":
*30478
```

Table 3.—Tape File Structure and Program Listings

```
201: "Statements 197-203":
202: "*S34":1.0032→r12
203: "D[H3+Instr+Std]":1.1115→r15
204: "(C13)+(O18-T)+(O18-C)+(O18-W)":
205: "45":1.00191→r18
206: "46":1.00045→r21
207: "STANDARDS":
208: ."Statements 204-212":
209: if r7=0;5.4→r13;gto "S34"
210: if r7=9;U→U[2];1.64→r52;gto "C13"
211: if r7=18;gto "D"
212: if r47=27;U→U[1];38.6→r19;gto "O18-T"
213: if r47=36;U→U[1];28.16→r19;gto "O18-C"
214: if r47=45;U→U[1];38.6→r19
215: "Tank CO2-raw C-O":if r47=45;-36.52→r25;-25:48→r24;gto "O18-W"
216: "S34":
217: "ABUND":1.095→r11
218: r11*r12*(1+r13*1e-3)*U-r13→r14
219: wrt 16.2,C$,"(CDT) =",r14,"%.";wrt 16.1
220: gto "END"
221: "D":
222: r15*U→r16
223: wrt 16.2,C$,"(SMOW)=",r16,"%.";wrt 16.1
224: gto "END"
225: "C13":87621→r22
226: if U[1]=87621;dsp "Set Mass Spec for Oxygen";gto 16
227: if r30=87621;gto "O18-W"
228: "ABUND":1.0675→r17;.0337→r20
229: r17*(1+r52*1e-3)*r18*U[2]-r20*(1+r52*1e-3)*r21*U[1]+r52→r22
230: wrt 16.2,C$,"(PDB) =",r22,"%.";wrt 16.1
231: F$&"O18-C"→C$
232: if r23=87621;gto "O18-C"
233: gto "END"
234: "O18-C":87621→r23
235: if U[2]=87621;dsp "Set Mass Spec for Carbon";gto 16
236: "ABUND":1.0014→r17;.009→r20
237: r17*(1+r19*1e-3)*r21*U[1]+r20*(1+r19*1e-3)*r18*U[2]+r19→r23
238: wrt 16.2,C$,"(SMOW)=",r23,"%.";wrt 16.1
239: F$&"C(13)"→C$
240: if r22=87621;gto "C13"
241: gto "END"
242: "O18-T":
243: "ABUND":1.0014→r17;.009r20:
244: "C-RAW":-27.29→r22
245: r17*(1+r19*1e-3)*r21*U[1]+r20*(1+r19*1e-3)*r18*r22+r19→r23
246: wrt 16.2,C$,"(SMOW)=",r23,"%.";wrt 16.1
247: gto "END"
248: "O18-W":87621→r30;if U[2]=87621;ent "Do 9ou wish carbon analysis?",A$
249: if "yes"=A$;dsp "Set Mass Spec for Carbon";"   "→A$;gto 16
250: if 87621=U[2];-36.52→U[2]
*11230
```

Table 3.--Tape File Structure and Program Listings

```
251: "ABUND":1.0014→r17;.009→r20
252: 26.3524→V[1];27.0933→V[2];27.0933→V[3];28.3281→V[4];27.5872→V[5]
253: 26.3524→V[6];25.8584→V[7];25.6492→V[8];27.0839→V[9];28.7393→V[10]
254: "FRACTIONATION":1.0413→r26
255: "Gm Oxy Ratio":ent "Load Pressure (cmHg)?",W
256: ent "CO2-H2O Vessel No. ?",C
257: W/76→W;82.054*298/(W*V[C])→G;1/G→G
258: 2*G→G;.5551/G→r27
259: r21*U[1]→r31;r21*r24→r32;r18*r25→r33
260: r31/r27*(r26+r27)-r26/r27*r32→r28
261: r28*r17+r20*r33→r29
262: r29+r19+1e-3*r29*-r19→r30
263: 1/r26*(r30+1000)-1000→r30
264: wrt 16.2,C$,"(SMOW)=",r30,"%.";wrt 16.1
265: gto "END"
266: "CONST":ent "Constant X?",r31,"Constant Y?",r32;gto "END"
267: "TAB":ent "Temp-C",r33,"Mineral A[%.]",r34,"Mineral B[%.]",r35;gto "END"
268: "END":87621→U[1]→U[2];gto "START"
*5702
```

File 4:

File containing calibration data matrix

Table 3.—Tape File Structure and Program Listings

File 5:

Mass Spectrometer Program with Output to External Printer [11]

```
0: "W":dim H[40],X[20],M[40],D[40],B$[8],C$[8],D$[16],F,Q
1: dim A$[3],S[0:81],R[80],N[80],S$[16],C[40],E$[8],F$[1],R$[3]
2: dim J$[16],H$[3],E[20],G$[20],U[2],K[54,2],K$[54,12],T$[54,8],I$[32]
3: dim L$[3],A[80],P$[8],Z[1],Z$[5],V[10],O$[4],N$[92],W$[7,12],V$[8]
4: ldf 4,K[*],K$,T$
5: buf "Dump",I$,1
6: 87621→U[1]→U[2]
7: dsp "MASS SPEC DATA REDUCTION PROGRAM";stp
8: ent "Day-Date(eg=Mon_12/27/77)",D$
9: ent "Standard Used:[8 characters]",B$
10: ent "On which side is standard gas ?",E;jmp 4
11: "START":dsp "New Sample";1→M;wrt 11,char(12)
12: beep;wait 250;jmp (M+1→M)>50
13: 1→M;stp
14: ent "Lab Number ?",S$,"Sample Name",J$
15: jmp 2
16: fmt 1,/,/;wrt 11.1;stp
17: char(18)→F$
18: ent "Which Stable Isotope Analysis:",C$
19: F$&C$→C$
20: ent "EA=",r4,"VRE=",r5,"IR=",r6
21: ent "Setting:Decade A ?",A,"Setting:Decade B ?",B
22: jmp 2
23: fmt 1,/,/;wrt 11.1
24: ent "No. Data Sets Per Side[min=3]",r40,"Repetition No.",R
25: ent "[IR] Multiplier",Z[1];2r40*(R+1)→I
26: if I>80;dsp "Array Overload";wait 5000;jmp -2
27: ent "Machine Time?",E$
28: "ALL":fmt 1,95"x";fmt 3,95"-";fmt 2,c7,c9,4x,c16,10x,c12,10x,c5,3x,c8
29: fmt 6,5x,"STATUS:",10x,"EA(V) VRE(mv) IR",10x,"SETS REPS MPLY"
30: fmt 7,c8,4x,"Standard=",2x,c8,4x,"Side=",f1.0,5x,c9,f7.4,5x,c9,f7.4
31: fmt 9,/,30x,"Calibration Run"
32: wrt 11.1;wrt 11.2,"Sample=",S$,J$,D$,"Time=",E$;wrt 11.3
33: wrt 11.6;fmt 6,24x,f2.0,4x,f3.0,4x,f1.0,11x,f2.0,4x,f1.0,3x,f3.1
34: wrt 11.6,r4,r5,r6,r40,R,Z[1];wrt 11.3
35: wrt 11.7,C$,B$,E,"Decade A=",A,"Decade B=",B
36: wrt 11.1
37: ent "Any Corrections ?",L$;if L$="yes";spc 4;gto "START"
38: if C$=F$&"S(34)";0→r7
39: if C$=F$&"C(13)";9→r7
40: if C$=F$&"D/H";18→r7
41: if C$=F$&"O(18)-T";27→r7→r47
42: if C$=F$&"O(18)-C";36→r47;27→r7
43: if C$=F$&"O(18)-W";45→r47;27→r7
44: if r5=10;r7+r6→r8
45: if r5=30;r7+r6+3→r8
46: if r5=100;r7+r6+6→r8
47: Z[1]*K[r8,1]→F;1/Z[1]*K[r8,2]→Q
48: abs(val(E$)-val(T$[r8]))→r38
49: if r38>400;"yes"→A$;dsp "Calibration Update Required";wait 5000;jmp 2
50: ent "Is this calibration ?",A$
*3809
```

Table 3.—Tape File Structure and Program Listings

```
51: if A$="yes";wrt 11.9;wrt 11.1;jmp 2
52: jmp 2
53: dsp "[IR] Multiplier to 1X Position";stp
54: if A$#"yes";jmp 7
55: ent "Decade A=",r45,"Decade B=",r46
56: fmt 2,"Decade A=",f7.4,5x,"Decade B=",f7.4
57: ent "No.Data Sets Per Side[min=3]",r40,"Repetition No.",R
58: ent "[IR] Multiplier",Z[1];2r40*(R+1)→I
59: if I>80;dsp "Array Overload";wait 5000;jmp -2
60: wrt 11.2,r45,r46;wrt 11.1
61: "SIDE    "→V$;"REP.0          "→W$[1];"REP.1          "→W$[2]
62: "REP.2         "→W$[3];"REP.3          "→W$[4];" AVG. NUM.  "→W$[5]
63: " STD. DEV.  "→W$[6];"2 SIGMA(%.) "→W$[7]
64: fmt 4,/,/,c8,7c12
65: wrt 11.4,V$,W$[1],W$[2],W$[3],W$[4],W$[5],W$[6],W$[7]
66: wrt 11.1
67: fmt 9,c92
68: "ENT":dsp "Verify Mass Spec Status";wait 5000
69: dsp "When Ready, Push Start-Reset[IR]"
70: wtc 3,32
71: "REC":1→K;0→T;0→r1;1→S[0];0→H;""→N$
72: for J=1 to I
73: buf "Dump";if J=2;dsp ""
74: tfr 3,"Dump"
75: if len(N$)=92;wrt 11.9,N$;wrt 11.3;""→N$
76: jmp rds("Dump")=16
77: red "Dump",G$
78: 2→S[J];if G$[1,1]="-";1→S[J]
79: val(G$[2,9])→N[J];G$[2,9]→P$
80: val(G$[15,15])→R[J]
81: if val(G$[14,14])=8;0→N[J];"Overload"→P$
82: if G$[11,11]="+";0→N[J];"NegError"→P$
83: H+1→H
84: "RET":fxd 0
85: gto "TWO";if R[J]=0;gto "ONE"
86: "ONE":str(S[J])→N$[1,4];O$→N$[5,8];P$&O$→N$[9,20];fxd 6
87: "----------  ----------  ----------  "→N$[21,56];jmp 5
88: "TWO":fxd 6;jmp R[J]
89: "----------  "→N$[21,32];if R[J]=1;P$&O$→N$[21,32]
90: "----------  "→N$[33,44];if R[J]=2;P$&O$→N$[33,44]
91: "----------  "→N$[45,56];if R[J]=3;P$&O$→N$[45,56]
92: if A$#"yes";jmp 5
93: if R#R[J];jmp 4
94: 1→M
95: beep;wait 50;jmp (M+1→M)>20
96: 1→M
97: N[J]+T→T
98: if N[J]>0;r1+1→r1
99: gto "CONT";if H=R+1;gto "AVG"
100: "AVG":if r1=0;prt "*****ABORT******";gto "ENT"
*12125
```

Table 3.--Tape File Structure and Program Listings ...

```
101: 0→H;fxd 6
102: T/r1→r2;0→N
103: str(r2)→N$[57,68]
104: if R=0;"----------  ----------  "→N$[69,92]
105: if R=0;gto 112
106: for Y=0 to R
107: if N[J-Y]=0;jmp 2
108: (N[J-Y]-r2)↑2+N→N
109: next Y
110: √(N/(r1-1))→N;str(N)→N$[69,80]
111: str(2N/F)→N$[81,92];if A$="yes";"----------  "→N$[81,92]
112: r2→C[K];S[J]→A[K];K+1→K;0→T→r1
113: "CONT":next J
114: wrt 11.9,N$;wrt 11.3;""→N$
115: if A$="yes";gto "CAL"
116: if E=1;A→r1;B→r2;jmp 2
117: if E=2;B→r1;A→r2
118: fmt 1,95"#";wrt 11.1
119: fmt 2,"Date of Last Calibration",5x,c12;wrt 11.2,K$[r8]
120: fmt 2,"One permil=",f10.7,5x,"Calibration factor 'q' =",f10.8
121: wrt 11.2,F,Q
122: wrt 11.1
123: 0→M→N
124: for J=1 to K-2
125: abs(C[J]-C[J+1])→M[J];M+M[J]→M
126: next J
127: M/(K-2)→M
128: for J=1 to K-2
129: N+(M[J]-M)↑2→N
130: next J
131: √(N/(K-3))/√(K-2)/F→P
132: for J=1 to K-1
133: if A[J]=1;A+Q*C[J]→H[J];jmp 2
134: if A[J]=2;B+Q*C[J]→H[J]
135: next J
136: sfg 4
137: if E=2;cfg 4
138: 1→L;E→r10;0→D
139: for J=1 to K-3
140: Q*((C[J]+C[J+2])/2-C[J+1])→r9
141: if flg4;-r9→r9
142: cmf 4
143: (r2-r1+r9)*1000/H[r10]→D[L]
144: if J=1;r10+2→r10;0→I
145: if I=2;r10+2→r10;0→I
146: I+1→I
147: D[L]+D→D;L+1→L
148: next J
149: cfg 4;D/(L-1)→U
150: 0→S
*5381
```

Table 3.--Tape File Structure and Program Listings

```
151: for J=1 to L-1
152: (D[J]-U)↑2+S→S;next J
153: r(S/(L-2))→S
154: sfg 4
155: if E=2;cfg 4
156: 1→I;0→X
157: for J=1 to K-3
158: .5(H[J]+H[J+2])/H[J+1]→X[J]
159: if flg4;1/X[I]→X[I]
160: cmf 4
161: X+X[I]→X;I+1→I
162: next J
163: X/(I-1)→X;0→V
164: for J=1 to I-1
165: (X[J]-X)↑2+V→V
166: next J
167: r(V/(I-2))→Z
168: (X-1+2Z/r(I-1)-(X-1))1000→T
169: fmt 1,95"#";fmt 2,95"-"
170: "Delta(IR) Precision         Alpha[X-std]    Mean [Ind.Meas.]"→N$[1,58]
171: "     Std.Dev.       2 Sigma of Mean  "→N$[59,92]
172: fmt 3,c92;wrt 11.3,N$
173: fmt 4,5x,f8.6,x,"%.",31x,f9.6,6x,f8.6,5x,f11.6,x,"%."
174: wrt 11.4,P,X,Z,T
175: wrt 11.2
176: fmt 5,2x,c8,4x,"Delta[Raw]=",f10.4,x,"%.",4x,"(Std.Dev.)=",f8.5,x,"%."
177: wrt 11.5,C$,U,S
178: wrt 11.1
179: gto "E"
180: "CAL":0→L
181: r45→r1;r46→r2
182: for J=1 to K-2
183: abs(C[J]-C[J+1])+L→L
184: next J
185: L/(K-2)→r48;r2-r1→r49;(r1+r2)/2→r50
186: 1000r49/r50→r51;abs(r48/r51)→F;abs(r49/r48)→Q
187: fmt 1,95"#";wrt 11.1
188: fmt 2,"New Calibration:  Date",3x,c16;wrt 11.2,D$
189: fmt 3,5x,"One permil=",f10.7,5x,"Calibration factor 'q' =",f10.8
190: wrt 11.3,F,Q;wrt 11.1
191: ent "Save Cal ?",R$;if R$#"yes";jmp 3
192: F→K[r8,1];Q→K[r8,2];D$→K$[r8];E$→T$[r8]
193: rcf 4,K[*],K$,T$
194: ent "Do you wish analysis ?",R$
195: gto "END";if R$="yes";"   "→A$;gto 24
196: "E":
197: "Calibration Routines":
198: fmt 1,95"#"
199: fmt 2,/,c8,x,c7,2x,f9.4,x,c2,2x,/
200: "INSTRUMENTAL":
*9695
```

Table 3.—Tape File Structure and Program Listings

```
201: "Statements 200-206":
202: "*S34":1.0032→r12
203: "D[H3+Instr+Std]":1.4485→r15
204: "(C13)+(O18-T)+(O18-C)+(O18-W)":
205: "45":1.00259→r18
206: "46":1.00092→r21
207: "STANDARDS":
208: "Statements 207-215":
209: if r7=0;5.4→r13;gto "S34"
210: if r7=9;U→U[2];1.64→r52;gto "C13"
211: if r7=18;gto "D"
212: if r47=27;U→U[1];38.6→r19;gto "O18-T"
213: if r47=36;U→U[1];28.16→r19;gto "O18-C"
214: if r47=45;U→U[1];38.6→r19
215: "Tank CO2-corrected-O:C":if r47=45;11.7468→r24;-36.6231→r25;gto "O18-W"
216: "S34":
217: "ABUND":1.095→r11
218: r11*r12*(1+r13*1e-3)*U-r13→r14
219: wrt 11.2,C$,"(CDT) =",r14,"%.";wrt 11.1
220: gto "END"
221: "D":
222: r15*U→r16
223: wrt 11.2,C$,"(SMOW)=",r16,"%.";wrt 11.1
224: gto "END"
225: "C13":87621→r22
226: if U[1]=87621;dsp "Set Mass Spec for Oxygen";gto 16
227: if r30=87621;gto "O18-W"
228: "ABUND":1.0675→r17;.0337→r20
229: r17*(1+r52*1e-3)*r18*U[2]-r20*(1+r52*1e-3)*r21*U[1]+r52→r22
230: wrt 11.2,C$,"(PDB) =",r22,"%.";wrt 11.1
231: F$&"O18-C"→C$
232: if r23=87621;gto "O18-C"
233: gto "END"
234: "O18-C":87621→r23
235: if U[2]=87621;dsp "Set Mass Spec for Carbon";gto 16
236: "ABUND":1.0014→r17;.009→r20
237: r17*(1+r19*1e-3)*r21*U[1]+r20*(1+r19*1e-3)*r18*U[2]+r19→r23
238: wrt 11.2,C$,"(SMOW)=",r23,"%.";wrt 11.1
239: F$&"C(13)"→C$
240: if r22=87621;gto "C13"
241: gto "END"
242: "O18-T":
243: "ABUND":1.0014→r17;.009r20:
244: "C-RAW":-27.29→r22
245: r17*(1+r19*1e-3)*r21*U[1]+r20*(1+r19*1e-3)*r18*r22+r19→r23
246: wrt 11.2,C$,"(SMOW)=",r23,"%.";wrt 11.1
247: gto "END"
248: "O18-W":87621→r30;if U[2]=87621;ent "Do you wish carbon analysis?",A$
249: if "yes"=A$;dsp "Set Mass Spec for Carbon";"   "→A$;gto 16
250: if 87621=U[2];-36.52→U[2]
251: "ABUND":1.0014→r17;.009→r20
252: 26.3524→V[1];27.0933→V[2];27.0933→V[3];28.3281→V[4];27.5872→V[5]
253: 26.3524→V[6];25.8584→V[7];25.6492→V[8];27.0839→V[9];28.7393→V[10]
254: "FRACTIONATION":1.0413→r26
255: "Gm Oxy Ratio":ent "Load Pressure (cmHg)?",W
256: ent "CO2-H2O Vessel No. ?",C
257: W/76→W;82.054*298/(W*V[C])→G;1/G→G
258: 2*G→G;.5551/G→r27
259: (r27+r26)/r27→r31;r26/r27→r32
260: r17*(1+r19*1e-3)*r21*U[1]+r20*(1+r19*1e-3)*r18*U[2]+r19→r33
261: r31*r33-r32*r24→r30
262: 1/r26*(r30+1000)-1000→r30
263: wrt 11.2,C$,"(SMOW)=",r30,"%.";wrt 11.1
264: gto "END"
265: "CONST":ent "Constant X?",r31,"Constant Y?",r32;gto "END"
266: "TAB":ent "Temp-C",r33,"Mineral A[%.]",r34,"Mineral B[%.]",r35;gto "END"
267: "END":87621→U[1]→U[2];gto "START"
*23911
```

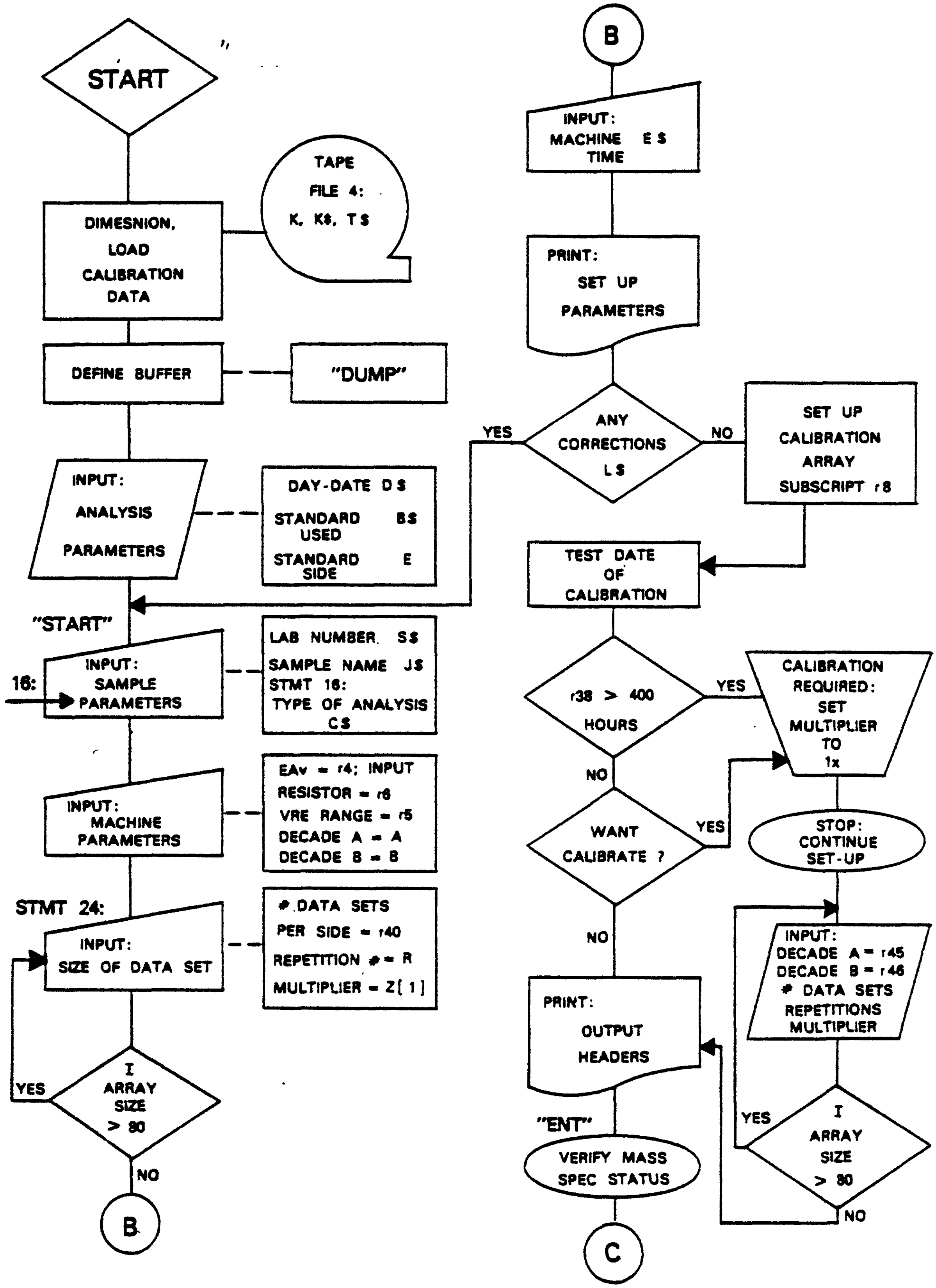

Figure 4.--Logic flow chart of mass spectrometer data reduction program.

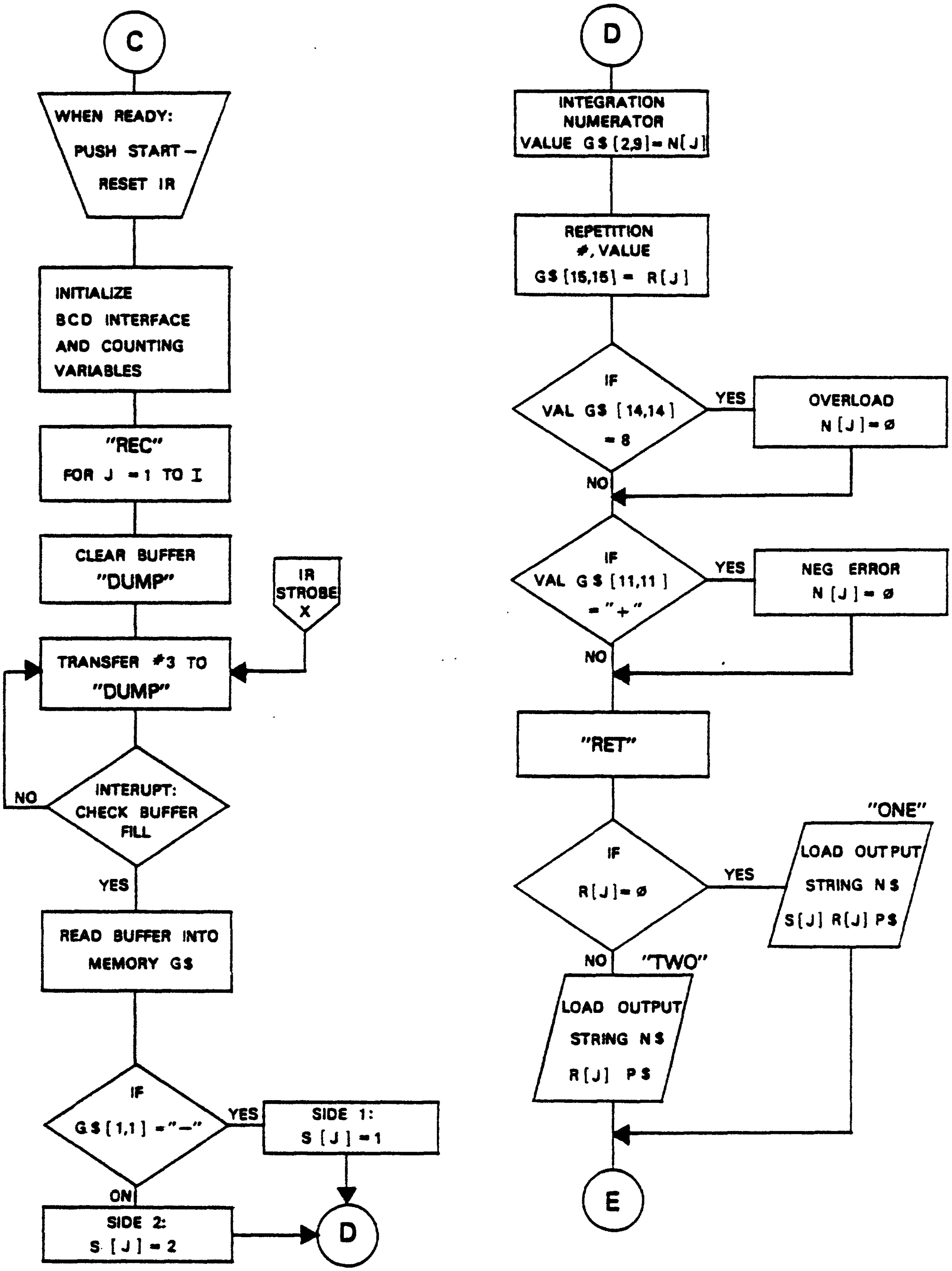

Figure 4.—Logic flow chart of mass spectrometer data reduction program.

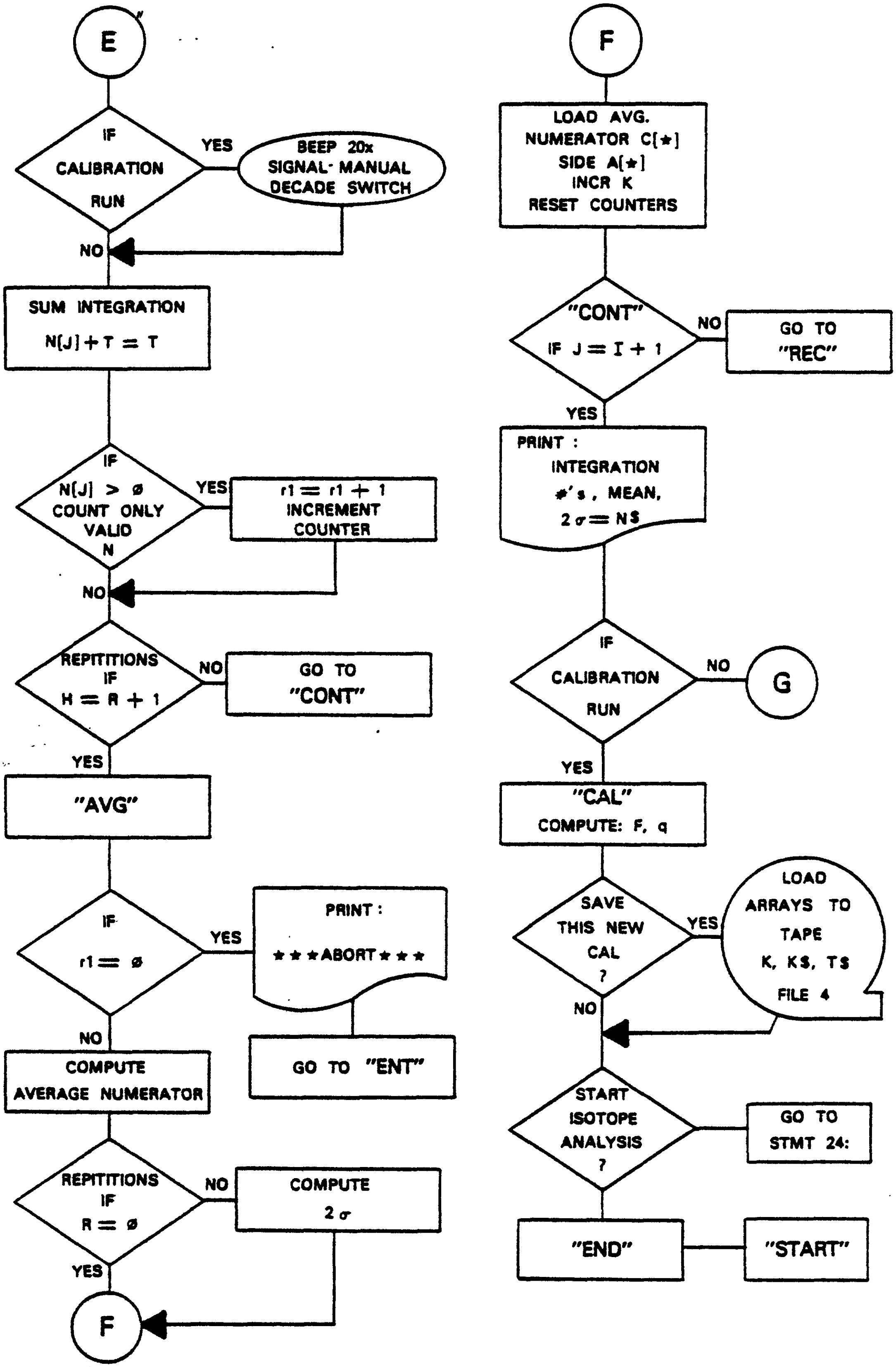

Figure 4.--Logic flow chart of mass spectrometer data reduction program.

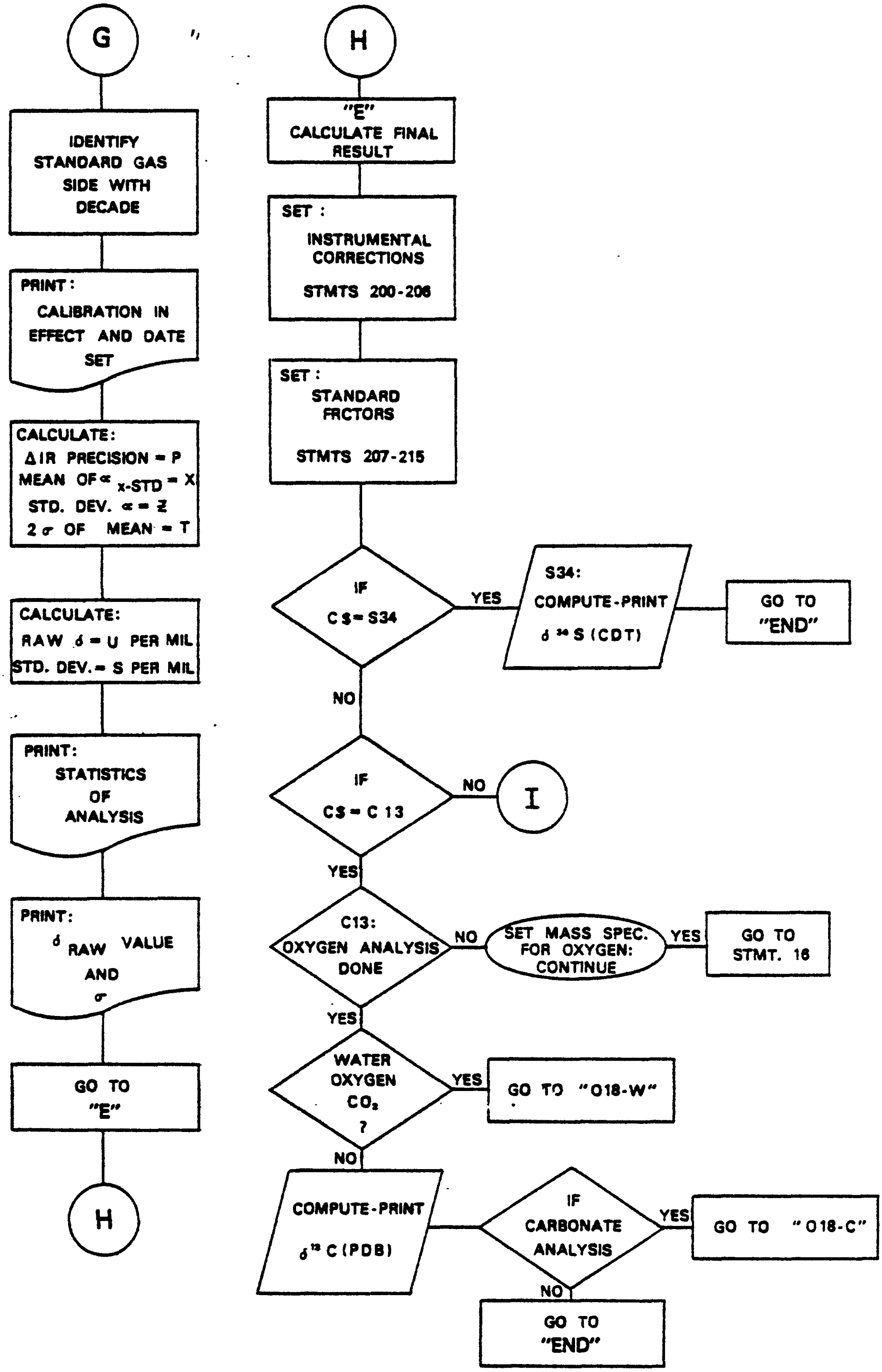

Figure 4.—Logic flow chart of mass spectrometer data reduction program.

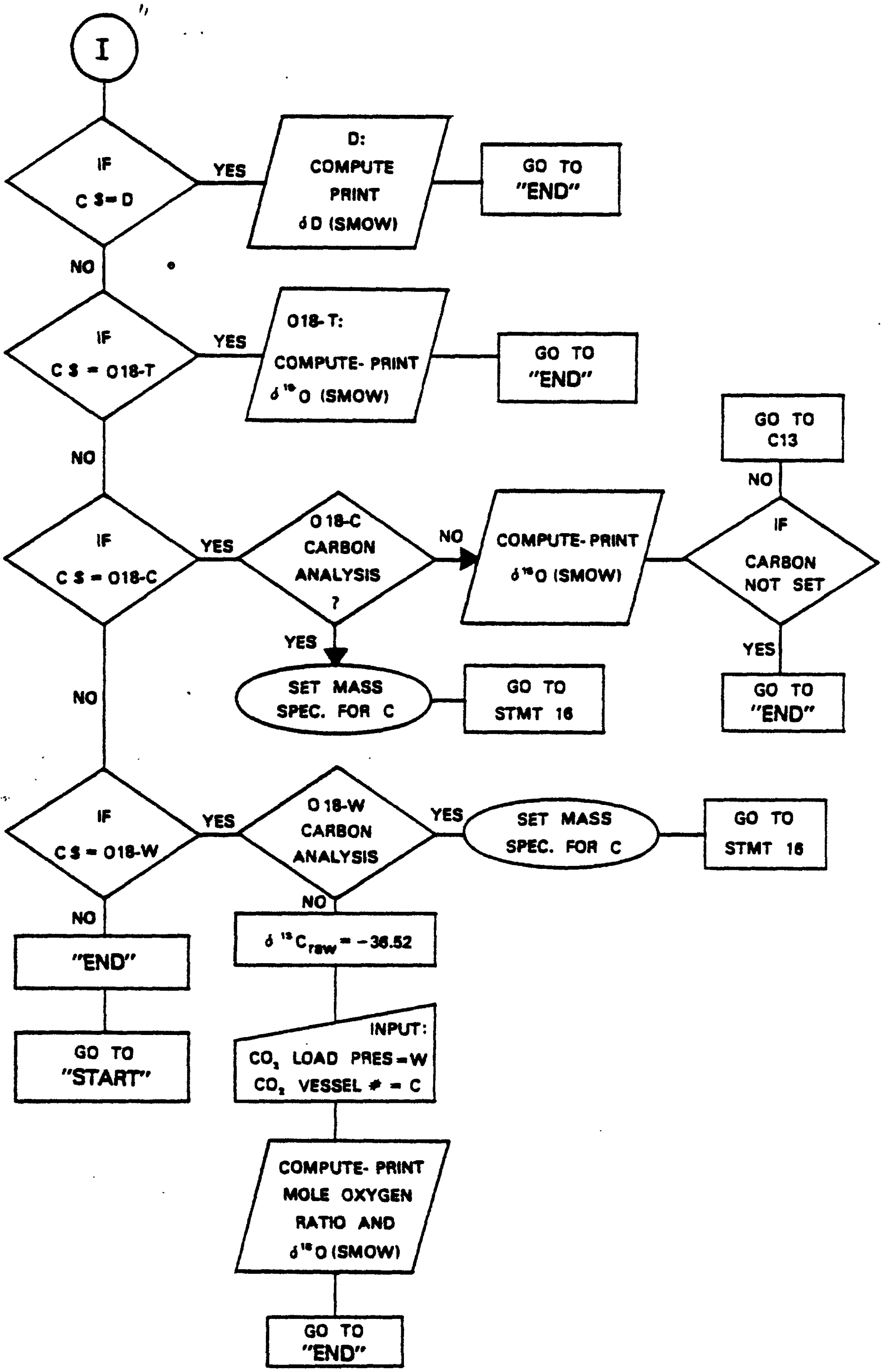

Figure 4.—Logic flow chart of mass spectrometer data reduction program.

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