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Report 2140

A COMPUTER-AIDED, EXTERNAL STANDARD TECHNIQUE FOR
SPECTROGRAPHIC ANALYSIS OF STAINLESS STEEL

April 1975

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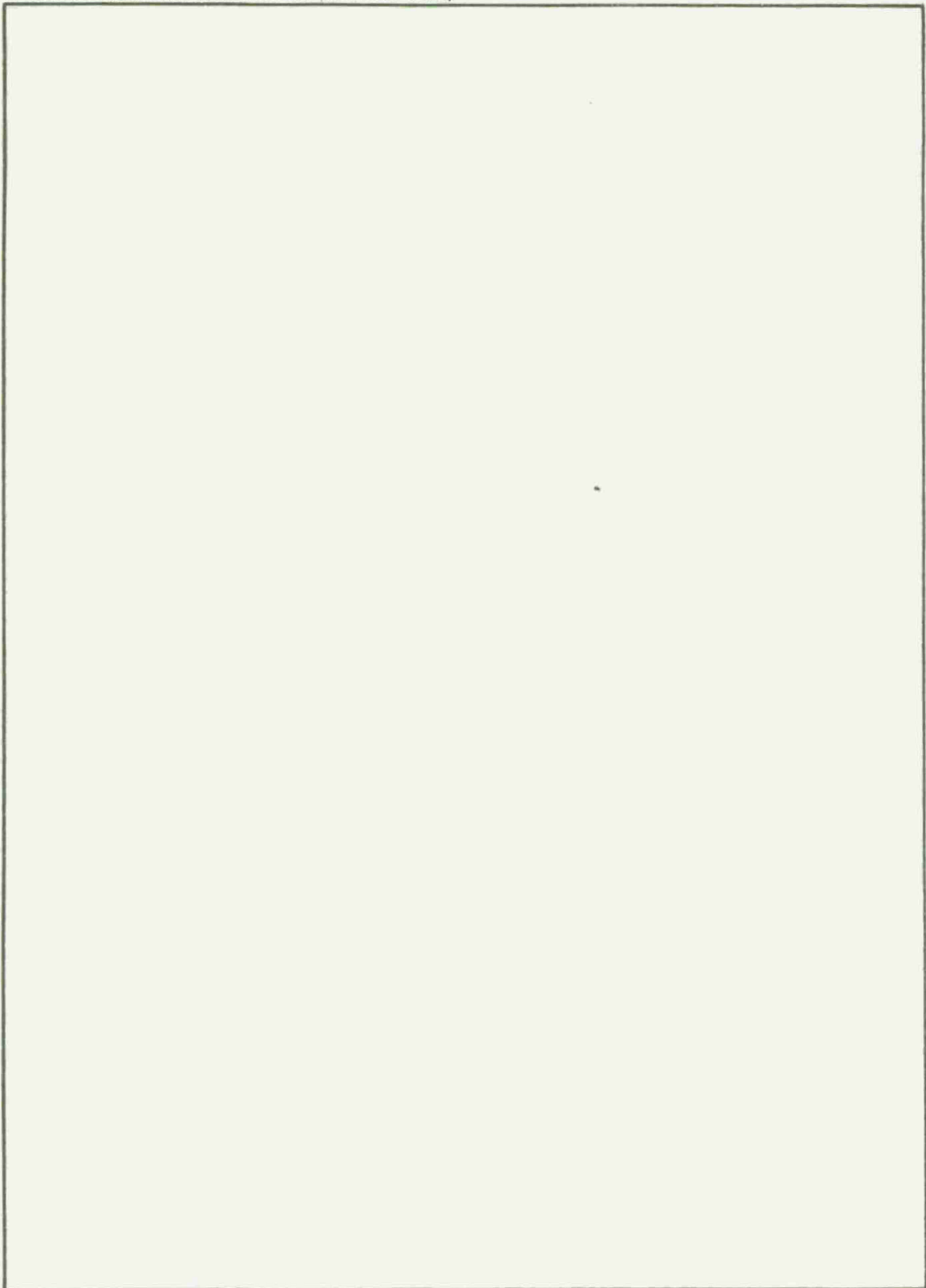
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FOREWORD

The work covered by this report was accomplished by Frank L. Harris under the direction of Emil J. York, Chief, Materials Engineering Division, Petroleum and Materials Department, U.S. Army Mobility Equipment Research and Development Center. The work constitutes a part of the U.S. Army Materials Testing Technology (MTT) program to provide better procedures in chemical, mechanical, and non-destructive testing techniques to increase inspection efficiency for material/materiel procured by the Army Materiel Command.

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A COMPUTER-AIDED, EXTERNAL STANDARD TECHNIQUE FOR SPECTROGRAPHIC ANALYSIS OF STAINLESS STEEL

I. INTRODUCTION

1. **Statement of the Problem.** The problem is to eliminate the necessity of knowing or determining the iron content of stainless steel materials which are being analyzed spectrographically in order to identify them or test their conformance to specifications.

2. **Background.** Quantitative spectrographic analysis of metals and alloys requires the determination of the ratio of intensity of a variable concentration component to that of a component whose concentration is constant within a group of several different specimens. In practice a group of samples, at least three or more, whose entire chemical content is known accurately, are used to prepare a calibration graph relating intensity ratio to percent concentration. Materials of unknown chemical content may then be analyzed by obtaining the intensity ratio for any given alloying element and reading the corresponding concentration from the calibration graph. For this technique to be useful, however, requires that the ratios be formed between the alloying elements and some other component (not being analyzed for) which is present at the same or very nearly the same concentration in all samples being analyzed, as well as in the standard samples used to construct the calibration graph.

Stainless steels and other highly alloyed materials exhibit a wide variation in chemical composition among various types. This fact makes it difficult or impossible to select a calibration set of three or more reference standards having a component common to all and at the same or nearly the same concentration level in all. This problem is sometimes dealt with by resorting to the concentration ratio technique; however, this method is often impractical in a service laboratory dealing with widely different nonroutine sample types for the following reasons:

a. The concentration ratio method requires the establishment of an absolute intensity of the internal standard element and an absolute intensity of each analysis element in each of a series of several standards. This must be done by averaging many repeated analyses of the standard series. These absolute intensities must be background-corrected.

b. Plots of the background-corrected intensity versus the concentration of the internal standard element and plots of background-corrected intensity versus concentration of each of the analysis elements must then yield absolute analytical graphs which are straight lines, parallel to one another, and of equal slope in order for the

concentration ratio method to be useful.

c. The concentrations of all elements in the standards, including those not being determined by emission spectroscopy must be known or determined.

This report describes a spectrographic method for stainless steel analysis which avoids the necessity of using the concentration ratio technique through the use of an external standard.

II. EXPERIMENTAL PROCEDURE

3. **Approach to the Problem.** Metallic iron (100 milligrams) was selected as an external standard. This material was added to the analysis gap as a powder contained in a graphite cup electrode. The stainless steel samples were in the form of discs, rods, or blocks having a flat surface area of at least 0.5 square inch and were used as self electrodes. The iron-filled graphite cup counter electrode was arced directly to the sample. The effect of the added iron was to cause the intensity of iron spectrum lines produced in the arc to have the same relative level from sample to sample in spite of large differences in iron content from sample to sample. A similar technique has been used for copper base alloys.¹

4. **Results.** A spectrographic procedure using an external standard technique was developed for the analysis of stainless steels. Working curves were established for chromium, nickel, manganese, silicon, and molybdenum. Eight replicate exposures were obtained on each standard to be used for each of the five elements to be determined, and the points were plotted according to ASTM recommended practice.² Examples of manually and computer-plotted calibration curves for chromium are shown in Figures 1 and 2. Figures 3 and 4 contain samples of output from the computer for the chromium analysis. The computer programs employed were written by personnel at the National Bureau of Standards (N.B.S.).³ After the working curves have been established, the analytical procedure is as follows:

- a. Obtain four replicate exposures on each sample.
- b. Determine the arithmetic mean of intensity ratios.

¹ F. L. Harris, "Effects of Extraneous Materials in the Uni-Arc," *Applied Spectroscopy*, 26, 3 (1972) p. 358.

² 1973 Annual Book of ASTM Standards, Part 32, Standard E 305-6F, p. 821.

³ S. D. Rasberry, M. Margoshes, and B. F. Scribner, National Bureau of Standards Technical Note 407 and Supplement, February 1968.

STAINLESS STEEL WORKING CURVE

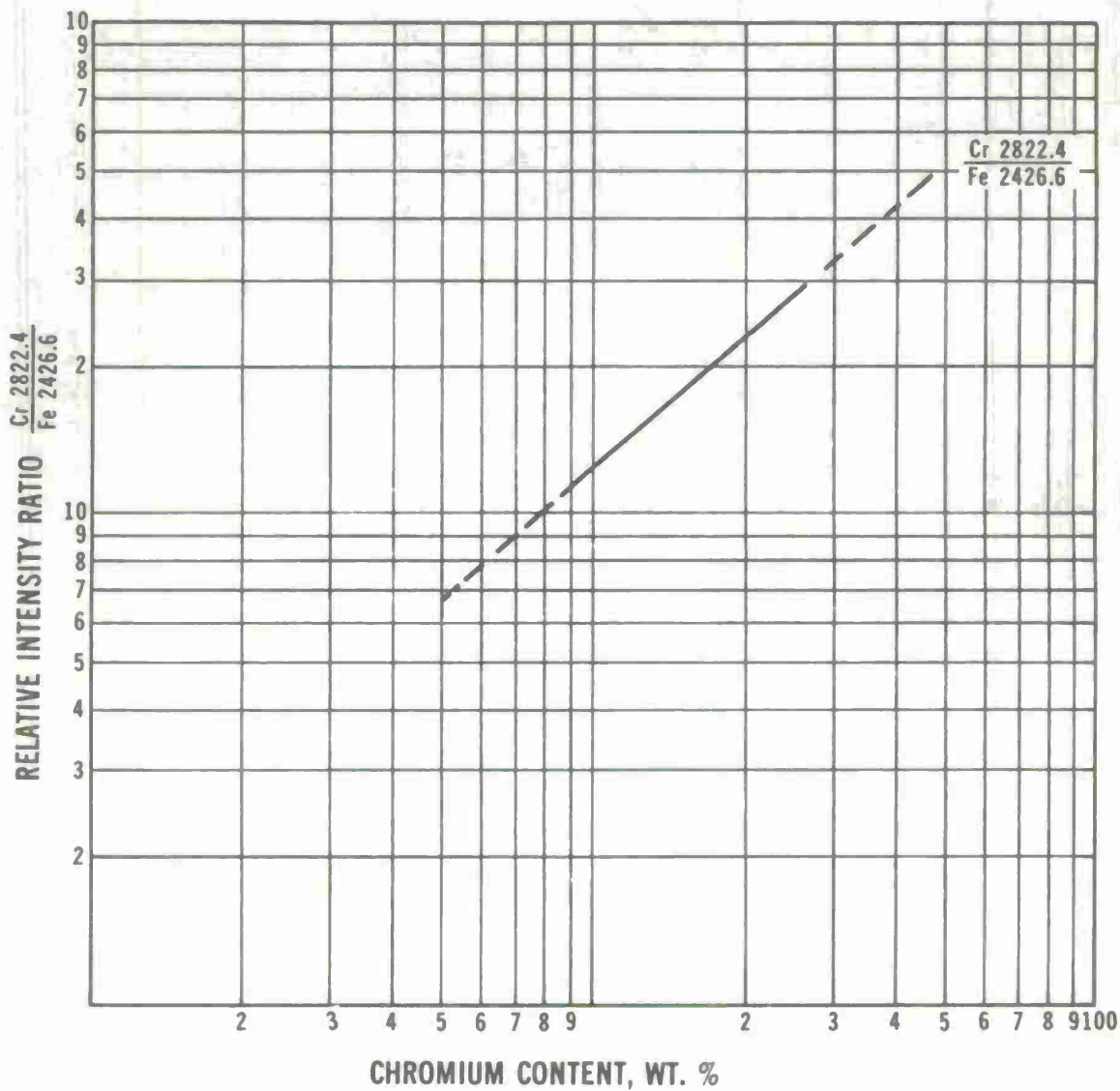


Figure 1. Manually plotted calibration curve for chromium analysis.



RANGE OF CONCENTRATION (ACROSS PAGE) =
8.82915 TO 21.6699 PERCENT

RANGE OF INTENSITY (DOWN PAGE) =
4.54012E-2 TO 2.11252

Figure 2. Computer-plotted calibration curve for chromium analysis.

RELATIVE INTENSITY RATIOS FOR CHROMIUM ANALYSIS
 ANALYSIS PAIR = CHROMIUM 2822.4/IRON 2926.6

PCT. T. ANAL. LINE	PCT. T. INT. STD.	INTENSITY ANAL. LINE	INTENSITY INT. STD.	INTENSITY RATIO
32	71.9	1.69533	.885532	1.91448
21.9	59	2.15292	1.07837	1.99646
18.5	49.3	2.38362	1.25032	1.90641
23.3	57.5	2.07271	1.10292	1.87929
19.5	48.2	2.30962	1.27221	1.81545
21.6	56.3	2.17109	1.12302	1.93326
19.1	48.5	2.33853	1.26618	1.84692
25.8	63.1	1.94568	1.01406	1.9187
24.8	62.9	1.99425	1.01711	1.96069
23.7	59.5	2.05108	1.07032	1.91633
18.8	52.1	2.36081	1.19711	1.97209
21.7	58	2.16499	1.09467	1.97776
18.8	51.8	2.36081	1.20265	1.963
12.3	37.1	3.02782	1.53576	1.97154
27.6	63.6	1.86476	1.00646	1.85279
18.3	51.4	2.39914	1.2101	1.9826
AVE. INTEN. RATIO	STD. DEV., INTEN. RATIO	COEF. VAR., INTEN. RATIO		
1.92549	5.43724E-2	2.82383		
END OF DATA	AT 2410			

Figure 3. Computer output from the program INTEN-2, used to compute intensity ratios. The 16 replicate results were from a typical laboratory sample.

DEGREE	INDEX OF DETN	STD ERROR OF Y		
1	.999167	3.96781E-2		
2	.952478	.299705		
3	1	0		
WHAT DEGREE DO YOU WANT TO USE? 1				
TERM	COEFFICIENT			
0	.882556			
1	1.39563			
INTEN.	CONC. GIVEN	CONC. FOUND	DIFF.	PCT. DIFF.
1.53688	13.31	13.9007	.590665	4.43775
1.9803	18.35	19.8007	1.45074	7.90596
2.11252	23.72	21.6699	-2.05012	-8.643
1.1102	9.09	8.82915	-.260846	-2.86959
DO YOU WANT PLOT OF CURVE? YES (1) OR NO (0)				
? 0				
DO YOU WANT RESULTS FOR SAMPLES, YES (1) OR NO (0) ? 1				
RESULTS FOR SAMPLES				
DO YOU WANT AVERAGES ONLY? YES (1) OR NO (2) ? 0				
INDIVIDUAL RESULTS FOR SAMPLES				
33	1.91448	18.8883	4	
33	1.99646	20.0266	4	
33	1.90641	18.7773	4	
33	1.87929	18.4056	4	
AVERAGES FOR SAMPLES				
SAMPLE NO.	AVE. INT.	AVE. CON.	STD. DEV.	NO. OF RUNS
33	1.92416	19.0244	.69928	4

Figure 4. Computer output for chromium analysis on a typical laboratory sample.

- c. Determine the deviation of each ratio from the mean, noting which is largest. This is a doubtful result.
- d. Determine the average deviation for a single result omitting the doubtful result in this calculation.
- e. If the ratio of the doubtful result to the average deviation is greater than 2.5, reject the doubtful result.

The equipment used in this work was a Jarrell-Ash 3.4 Meter Ebert mount spectrograph; however, any emission spectrograph having the proper wavelength coverage (2300 Angstroms to 3300 Angstroms) and adequate reciprocal linear dispersion (2.5 to 3.0 Angstroms/MM) could be used. Table 1 lists the analytical parameters used. Tables 2 and 3 summarize the precision of the method and give a comparison between results obtained with X-ray fluorescence and optical emission spectrography. Table 4 compares the precision data for chromium obtained by manual calculations to that obtained from the computer. The precision data were obtained from 16 replicate analyses of a typical stainless steel specimen similar in size and shape to the reference standards.

Table 1. Electrical and Photographic Parameters

	Electrical	Photographic
Capacitance	0.005 μ f	Spectrograph Jarrell-Ash 3.4 M Ebert
Inductance	310 μ h	Slit Size - 10 x 2000 Microns
Added resistance	None	Filter - 100/28 % T
rf current	3.5 amp	Emulsion SA No. 1
arc current	3.0 amp	Pre-Arc time 15 seconds
Analytical gap	3.0mm	Exposure time 18 seconds
Breaks/1/2 cycle	4	
Source type	Spark-ignited A.C. Arc	

The modification to INTEN-2, the program written by personnel at the National Bureau of Standards to determine relative intensity, is described by the flowchart in the Appendix. A list of additional variables is also found in the Appendix.

The data format for INTEN-2 has been modified as follows:

- a. The first data statement allows for the entry of string constants containing the names and wavelengths of the element being determined and the internal standards.

Example: 3592 DATA "CHROMIUM 2822.4", "IRON 2926.6"

Table 2. Precision Data

Element	Analysis Pair	Average Intensity Ratio	Coefficient of Variation (Percent)
Chromium	$\frac{2822.4}{2926.6}$	2.02	3.51
Nickel	$\frac{3012.0}{3091.5}$	3.92	7.09
Manganese	$\frac{2949.2}{2926.6}$	2.99	8.58
Molybdenum	$\frac{2816.2}{2926.6}$	1.13	8.05
Silicon	$\frac{2516.1}{2833.7}$	2.22	6.03

NOTE: Precision data were obtained from 16 replicate analyses of a stainless steel sample of similar shape and size as those used to establish the working curves. The precision is expressed in terms of the coefficient of variation among intensity ratios.

Table 3. Comparison Analyses

Element	X-Ray Fluorescence Spectrography (Percent)	Optical Emission Spectrography (Percent)
Chromium	18.80	19.00
Nickel	14.60	14.00

NOTE: The comparison analyses were done on a routine laboratory sample.

Table 4. Comparison of Precision Data for Intensity Ratios

Precision Parameters	Values Obtained	
	Manual	Computer
Arithmetic Mean	2.02	1.92549
Standard Deviation	0.071	0.0543724
Coefficient of Variation	3.51%	2.82383%

b. The second data statement enters a string constant containing only the name of the element being determined.

Example: 3595 DATA "CHROMIUM"

c. The only other modification to the data format is to alternate the entry of the data for the analytical line and the internal standard line, beginning with the analytical line.

Example:

```
3605 DATA 2822.4, 3, 21.5 62.4 14.7, 0
3610 DATA 2926.4, 3, 84.6, 80.9, 81.2, 0
```

Line 3605 enters the wavelength of the analytical line, the number of readings taken, and the readings themselves. Line 3610 enters the same information for the internal standards. Each data statement of this type must end with zero to indicate the end of the data entry for that particular line. A separate block of data beginning with the appropriate string constants must be provided for each element being determined

Sample

```
3592 DATA "CHROMIUM 2522.4", "IRON 2926.6"
3594 DATA "CHROMIUM"
3596 DATA 2, 3.57, 1
3598 DATA .563915, .543503
3600 DATA 1
3602 DATA 2822.4, 3, 39.9, 39.7, 46.9, 0
3604 DATA 2926.6, 3, 65.9, 67.9, 75.5, 0
3900 END
```

In the above sample, lines 3596 and 3598 are analogous to lines 900 and 901 in the data format of the unmodified program.

CONCLUSIONS AND DISCUSSION

5. Conclusions.

a. The internal standard dilution effect encountered in the spectrochemical analysis of highly alloyed materials such as stainless steels can be overcome by the use of an added external standard. This results in significant saving of time since it eliminates the necessity of knowing the iron content of the samples being analyzed.

b. The BASIC language program INTEN-2 can be modified to give the relative intensity ratio of an analysis pair rather than relative intensities alone. This makes the program useful for applications where it is required to reference the analytical line

to an internal or external standard line in order to overcome variations in exposure among separate spectra in a spectrographic analysis.

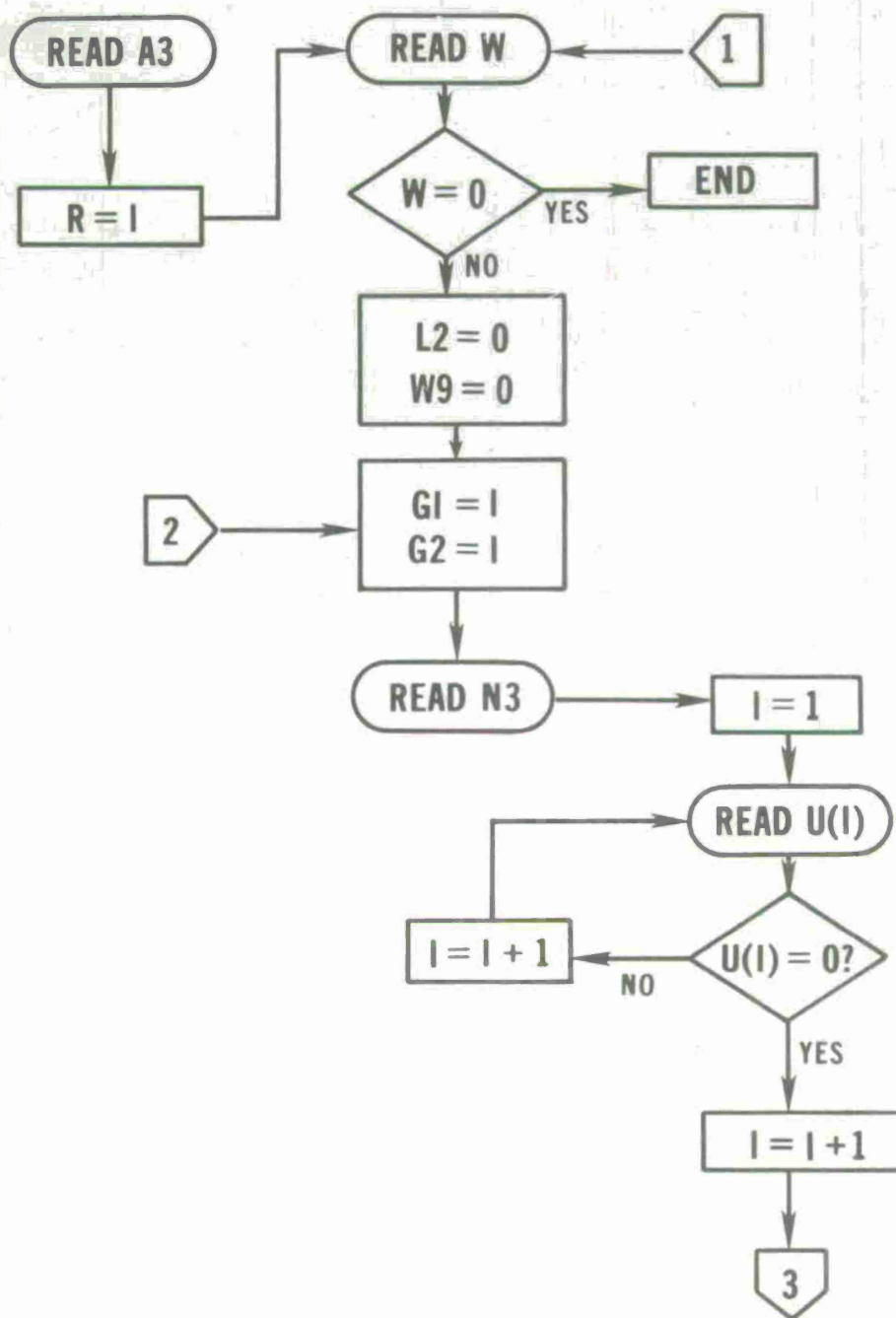
6. **Discussion.** An examination of the comparison data in Table 4 indicates a significant difference in results obtained by manual calculation and those output by the computer, the statistical terms from the computer having the more favorable magnitudes. Individual relative intensity values obtained with a calculating board using the Seidel Transform are quite different from those obtained with the computer using the Kaiser Transform. The intensity ratios, however, are the same whether obtained from the computer or the calculating board.

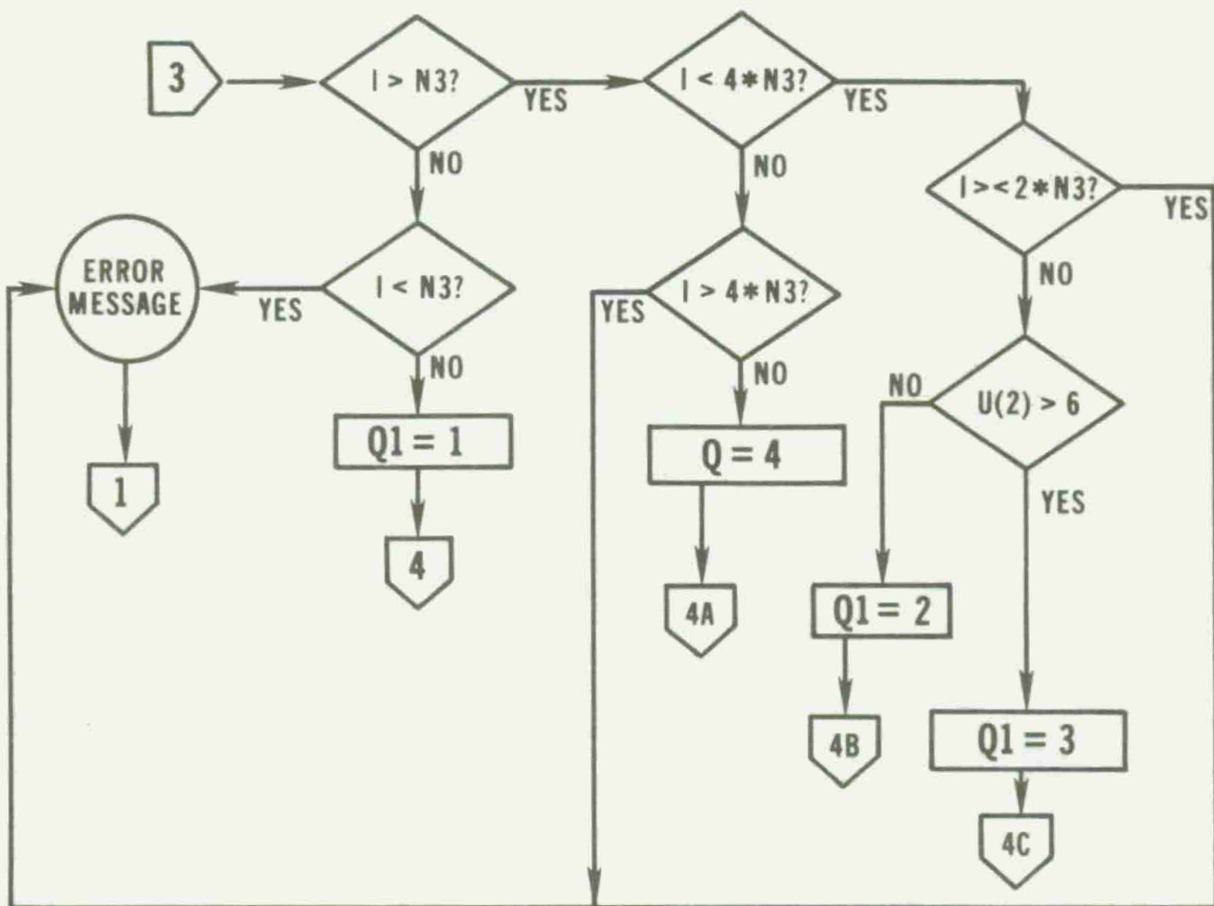
In addition to the changes to INTEN-2 shown in the flowchart in the Appendix, the data format has been altered to allow for the reading of the wavelength and transmission data of an external or internal standard line immediately following the reading of each analytical line.

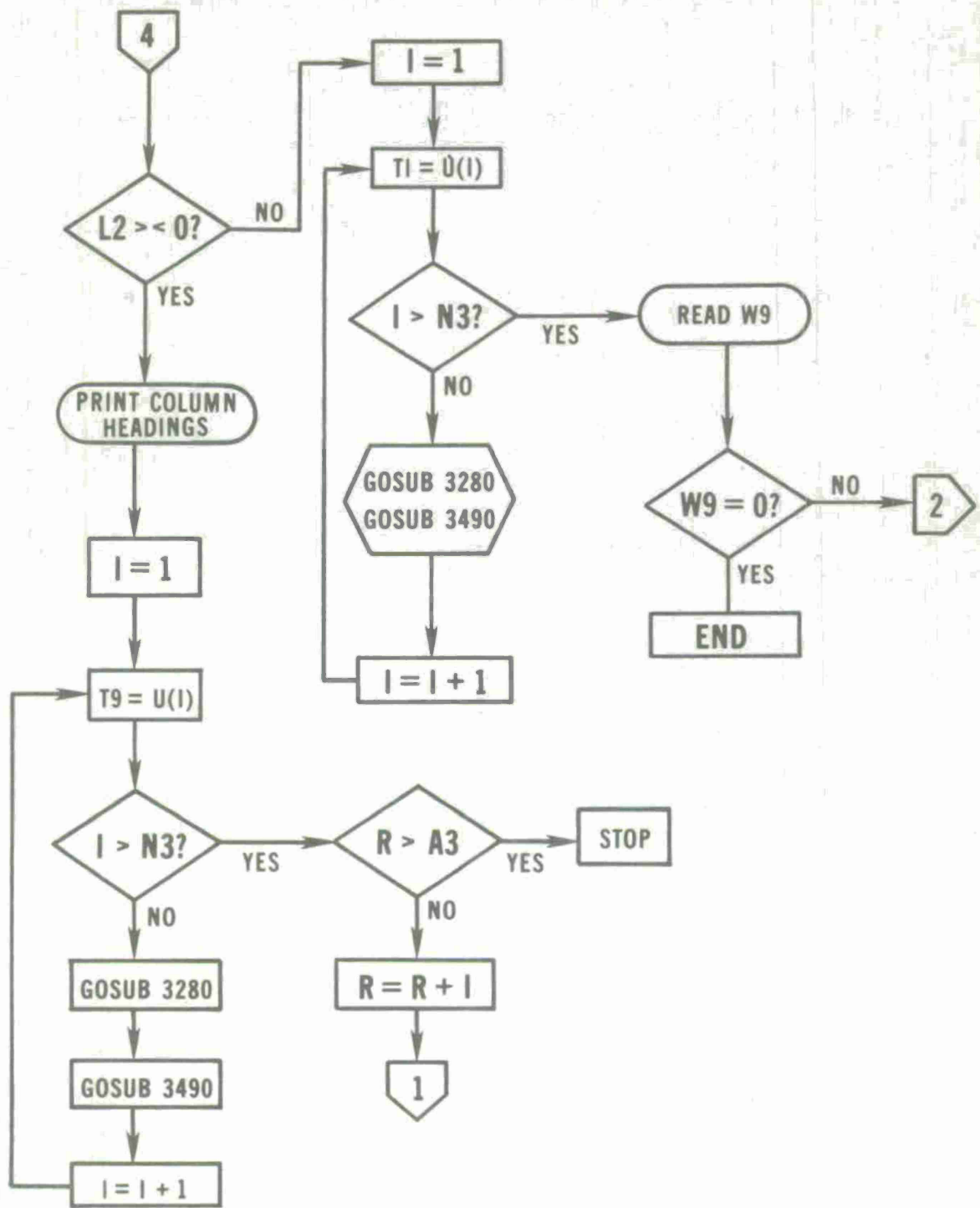
APPENDIX

FLOW CHART OF CHANGES TO INTEN-2

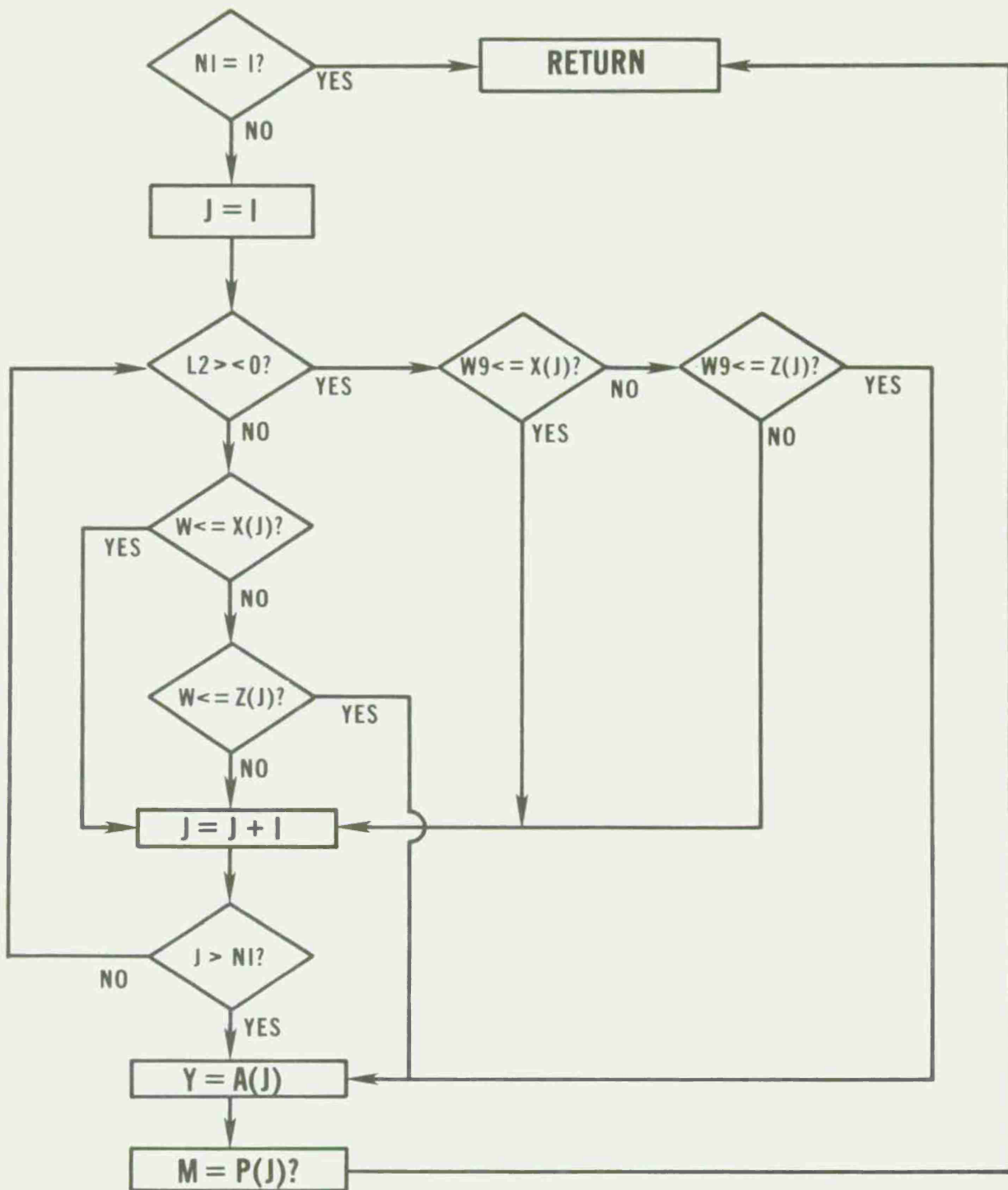
NOTE: The flow chart of changes to INTEN-2 shown here is partial, describing only the case where no step or background corrections are to be made. The logic, however, is the same in branches 4A, 4B, and 4C as in branch 4.



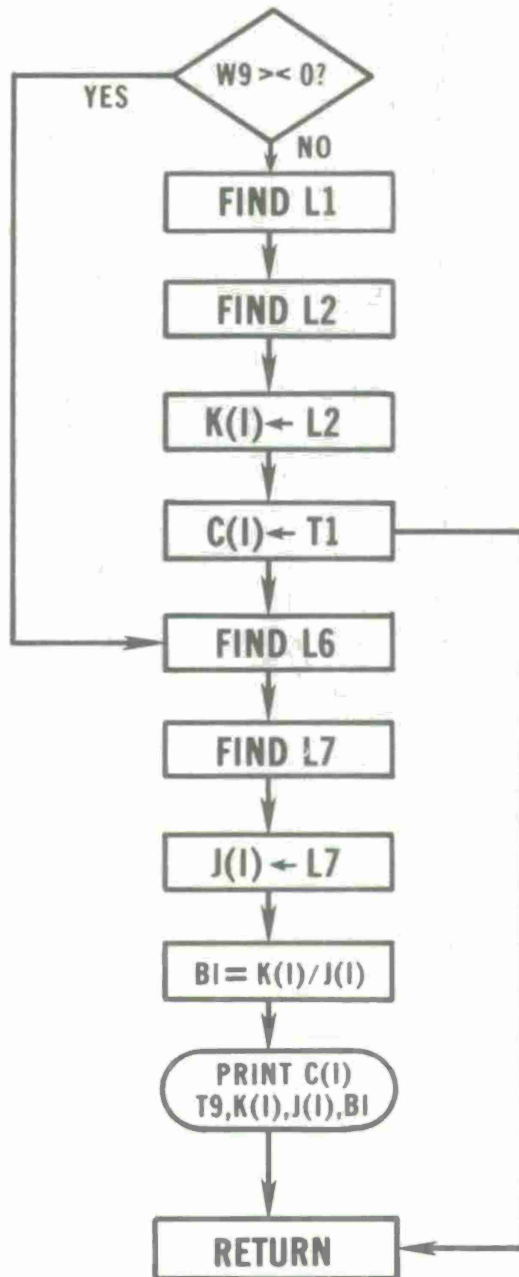




CHANGES TO CALIBRATION LOOKUP SUBROUTINE



CHANGES TO INTENSITY SUBROUTINE



List of Additional Variables Used with Modified INTEN-2

A	Average of intensity ratios
A3	Number of sets of analytical line – internal standard line pairs.
R	Loop counter
W9	Wavelength of internal standard line
S3	Sum of squares of intensity ratios
S	Sum of intensity ratios
N8	Dummy variable – Stores wavelength of internal standard
T9	Dummy variable – Stores transmission of internal standard
D1	Standard deviation among intensity ratios
V1	Coefficient of variation among intensity ratios
K(I)	Dummy variable to store uncorrected analytical line intensity in the intensity subroutine
C(I)	Dummy variable to store analytical line transmission in the intensity subroutine
L6	Uncorrected intensity of internal standard line
L7	Corrected intensity of internal standard
L8	Uncorrected background intensity near internal standard
L9	Corrected background intensity near internal standard
A\$	String variable – contains name and wavelength of element being determined
B\$	String variable – contains name and wavelength of internal standard element
E\$	String variable – contains name of element being determined
J(I)	Dummy variable used to store values of internal standard intensity in the intensity subroutine
B1	Intensity ratio
B2	Square of the intensity ratio

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