

By LAVERNE H. SCROGGINS (Eastern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, 600 E. Mermaid Lane, Philadelphia, Pa. 19118)

A collaborative study was conducted, using 2 types of automatic carbon-hydrogen-nitrogen analyzers. Thirty collaborators performed duplicate analyses on 6 samples with the duplicates being run on different days. Two collaborators sent a set of results for both types of apparatus. The samples studied were sulfadiazine, sulfanilamide, benzyl isothioureahydrochloride, nicotinic acid, stearic acid, and ethyl laurate. A critical factor was the choice of parameters or parameter combinations such as the catalyst used, combustion time, combustion temperature, reduction temperature, temperature differential between main and sub-ovens of the gas chromatographic column and detector unit, and use of on-line computer or electronic integrator. Evaluation of the data and overall consideration indicate that satisfactory results for carbon, hydrogen, and nitrogen may be obtained with either instrument. It is further indicated that certain conclusions will make possible an improvement in the results obtained by these apparatus. High combination temperature, low temperature differential between ovens, and the use of electronic integration of the detector response seem to be required for good accuracy and precision with the one apparatus. High temperature, longer combustion time, additional catalyst, and electronic integration led to better results with the other. It is, therefore, recommended that, before adoption as official first action, a second collaborative study be made, using the parameters indicated by this study.

The classical Pregl, Kjeldahl, and Dumas methods for microdetermination of carbon, hydrogen, and nitrogen have long demonstrated relatively good accuracy and precision in the analysis of most types of compounds. However,

the strong effects manual errors have on these classical techniques have been fully demonstrated. The Pregl method requires strict manual timing, good operator technique, and very rigid control of atmospheric conditions. The Dumas method is further dependent on obtaining high purity carbon dioxide and on complete removal of any interfering gases which would contribute to the volume of nitrogen.

New demands have led many laboratories to seek automation in their instruments to improve service to research by rapidly providing them with more reliable results. Total automatic control could result in a substantial improvement in reproducibility.

Analysts usually desire to exclude as many weighing steps as possible to minimize errors and reduce analysis time. Some laboratories are faced with increases in the number of samples and in the cost per analysis together with a lack of trained technicians. Moreover, minute yields are often received from preparative, paper, and thin layer chromatography and from synthetic processes where single compound concentration is limited. Several instruments rapidly analyze simultaneously for carbon, hydrogen, and nitrogen, using one small sample.

## METHOD

### *Instrumentation*

The 2 most popular apparatus which have incorporated automation of established techniques in the performance of organic elemental analysis are the Perkin-Elmer Model 240 elemental analyzer (PE) and the Hewlett-Packard F&M Model 185 CHN Analyzer (FM). The general guidelines for their operation follow the steps for the classical Pregl and Dumas methods, which involve: (A) the initial sample measurement; (B) sample transformation into gaseous carbon dioxide, water, and nitrogen; (C) separation of the gases formed; (D) measurement of the gases; and (E) calculation.

A.—The initial measurements are manual. Model

240 (PE) requires samples weighing 2–3 mg optimum and Model 185 (FM) requires the use of the Cahn balance to weigh accurately samples of 0.5–0.7 mg.

*B.*—The sample is placed in a port leading to the combustion train. The whole system is flushed with helium; in the PE apparatus, in addition, a measured volume of oxygen is introduced into the combustion chamber. The FM requires that a solid oxidation catalyst (oxides of manganese, tungsten, or silver) cover the sample and fill the sample container. The PE sample is automatically moved into the area by means of a magnet. The rod, whose tip contains the FM sample, must be manually thrust into the combustion chamber. The PE combustion tube filling consists of silver, silver vanadate, cupric oxide, and platinum; the FM filling is cupric oxide only. After the combustion is completed, the products are swept into the reduction tube where excess oxygen is removed, oxides of nitrogen are reduced, and interfering gases are adsorbed. This results in a final mixture of carbon dioxide, water, nitrogen, and the carrier gas, helium. The PE reduction tube filling is silver gauze and cuprin. The FM reduction tube contains reduced copper. All temperature settings may be adjusted by the analyst. The PE operates at a suggested combustion temperature of 900°C and a reduction temperature of 650°C. FM suggests a combustion temperature of 1050°C and a reduction temperature range of 400–500°C. The combustion process in both instruments proceeds automatically following preset time intervals.

*C.*—In the PE apparatus the combustion products are analyzed by sweeping them through a series of paired thermal conductivity cells. The total equilibrated combustion mixture present in the first cell is compared with the mixture in the second cell after it has gone through the water trap (magnesium perchlorate). The difference in composition effects a measurable voltage difference between the 2 cells. The water-free gas mixture is then carried to a third and fourth cell. The carbon dioxide is removed by the soda asbestos trap just before reaching the fourth cell. The voltage difference between cells 3 and 4 is a measure of the carbon dioxide present. The gas now entering the fifth cell contains nitrogen and helium. Its voltage difference is obtained by comparison with the sixth cell which contains helium only.

Separation of the product gases in the FM apparatus takes place in a gas chromatographic (GLC) column, allowing the gases to pass the detector singly. The column-detector unit is enclosed in an oven (temperature  $90 \pm 10^\circ\text{C}$ ) which has a shell (sub-oven) set to maintain a suggested temperature that is 5–15°C below the main oven. A

1°C variation in column temperature causes a 2% error in peak height.

*D* and *E.*—In the PE unmodified apparatus the readout obtained is programmed to a recorder. Normally in the FM apparatus the detector signals also pass to the recorder via an automatic sensitivity selector and an attenuator, which is tied in with the Cahn electrobalance. The peak heights are then made proportional to the per cent of the element in the sample. The proportionality constants are found by measuring the response as peak height or peak area produced by a known standard. Computations are normally done manually, using a calculator.

Both the PE and FM apparatus can be modified by changing the timing factors and tube fillings and by attaching an integrator, a digitizer, or an on-line computer for the final measurement and/or calculation. The procedure with attached integrator becomes more automated; time is saved (2 hr/day); accuracy and precision are increased. Other advantages are: (1) Higher sample weights may be used, (2) unweighed runs may be eliminated or reduced, and (3) blank runs and corrections may be reduced or eliminated. Thus, the overall versatility of the equipment is increased.

#### Experimental Design

Collaborators who used either a PE or an FM apparatus or both were given 6 samples: (1) sulfadiazine (2-sulfanilamidopyrimidine), (2) sulfanilamide (*p*-aminobenzenesulfonamide), (3) *S*-benzyl (benzyl isothioureia hydrochloride), (4) nicotinic acid, (5) stearic acid, and (6) ethyl laurate. They were instructed to make 2 analyses of each, using their own method under their normal working conditions. They were asked to analyze the duplicate sample on a second day and to describe any changes in original instrumentation as well as any deviation in procedure from that described in their instrument manual. The collaborators were also asked to fill out an enclosed questionnaire designed to determine details of the procedures which might vary from laboratory to laboratory.

#### Reagents

(See instrument instruction manuals (1, 2).)

(a) *Catalyst.*—Necessary for FM apparatus; optional for PE apparatus.

(b) *Standard.*—Equivalent to NBS microchemical standard.

#### Apparatus

(a) *Automatic CHN analyzer.*—Equivalent to F&M Model 185 CHN Analyzer or Perkin-Elmer 240 Analyzer.

(b) *Helium cylinder.*

(c) *Oxygen cylinder.*—PE apparatus.

(d) *On-line computer or integrator*.—Recommended.

(e) *Helium preheater and purifier*.—Optional.

(f) *Line voltage regulator*.—Optional.

#### Determination

Prepare and assemble apparatus as suggested in analyzer manual. Adjust helium flow. Adjust detector ovens and combustion-reduction furnace temperatures, and equilibrate to constant temperatures as directed. Adjust bridge current. Burn 2 unweighed samples of ca 2 mg (PE) or 0.6 mg (FM) to condition apparatus. Make at least 2 blank runs (simulated sample runs without sample) to check and adjust timing of each phase where necessary and to check pattern of final measurements. Run standard compound (PE, weighed to nearest 0.001 mg or better; FM, to nearest 0.0001 mg) and calculate factors as suggested in the manual. Initially check factors by running a known pure compound until 2 analyses are within 0.3% of the theoretical value. Analyze sample and calculate per cent, using standard carbon, hydrogen, and nitrogen factors.

#### Results and Discussion

Thirty collaborators reported carbon, hydrogen, and nitrogen data. Collaborators 15 and 18 reported data with both types of apparatus. Seven collaborators made use of integrators and 2 used computers for the final measurements and calculations. Acetanilide was the most widely used standard. Twenty-seven of the 30 collaborators used either acetanilide or cyclohexanone 2,4-dinitrophenyl hydrazone as the standard to analyze most of their samples. The following standards were used successfully by various collaborators for 1 or 2 of their compound analyses:

azobenzene, S-benzyl, cholesterol, dimethyl glyoxime, dioctyldiphenamine, glutaric acid, hexadecanol, phenacetin, 1-phenyl-2-thiourea, and thiocarbanilide.

Tables 1–6 contain the following information for each of the 6 samples studied: mean, difference between duplicate values, and deviation of mean from theoretical value. The statistics in Tables 7 and 8 summarize these data for all 6 compounds and compare data received from the 2 apparatus. The overall average deviation of the mean from the theoretical value for carbon for all the samples analyzed with the PE apparatus is less than 0.30 for all samples except the liquid, ethyl laurate. The total carbon bias for each of the first 4 compounds (sulfadiazine, sulfanilamide, S-benzyl, and nicotinic acid) was negative while the bias for stearic acid and ethyl laurate was positive. The size and sign of the biases probably depend, to a large extent, on the purity and combustion characteristics of the standard used. Examination of the data in Table 8 shows that the precision obtained for both hydrogen and nitrogen with the 2 apparatus was similar. There were also no marked differences in bias or average deviation of the mean from the theoretical value between the 2 apparatus.

Within-laboratory precision, calculated from the difference between duplicates, bias, and average deviation of the mean from theoretical value are shown in Table 9. Also shown is the average deviation when long chain compounds, stearic acid and ethyl laurate, are not included. This considerably improves the average deviation

Table 1. Collaborative results for sulfadiazine<sup>a</sup>

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
1 FM	48.00	3.98	22.18	0.06	0.10	0.09	0.01	-0.05	-0.20
2 FM	47.86	4.04	22.44	0.03	0.03	0.03	-0.13	0.01	0.06
3 PE	47.71	3.86	22.72	0.00	0.08	0.09	-0.28	-0.17	0.34
4 FM	48.00	4.08	22.45	0.28	0.09	0.26	0.01	0.05	0.07
5 PE	48.13	4.14	22.52	0.26	0.05	0.07	0.14	0.11	0.14
6 FM	49.48	4.18	22.11	2.28	0.15	0.00	1.49	0.15	-0.27
7 FM	48.04	4.02	22.46	0.20	0.01	0.27	0.05	-0.01	0.08
8 PE	47.53	3.96	22.75	0.43	0.02	0.06	-0.46	0.07	0.37
9 PE	47.70	4.06	22.68	0.17	0.07	0.10	-0.29	0.03	0.30
10 PE	47.98	4.03	22.50	0.04	0.06	0.22	-0.01	0.00	0.12
11 PE	47.86	4.02	22.39	0.11	0.00	0.04	-0.13	-0.01	0.01
12 PE	47.92	3.88	22.63	0.10	0.18	0.02	-0.07	-0.15	0.25
13 PE	48.20	4.04	22.59	0.27	0.10	0.20	0.21	0.01	0.21
14 FM	48.20	3.85	22.38	0.18	0.08	0.17	0.21	-0.18	0.00
15 FM	47.96	4.13	22.32	0.19	0.12	0.19	-0.03	0.10	-0.05

Table 1. (Continued)

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
15 PE	47.22	4.17	22.62	0.12	0.04	0.10	-0.77	0.14	0.24
16 FM	47.58	3.92	22.08	0.59	0.63	0.52	-0.41	-0.11	-0.30
17 PE	48.20	4.04	22.47	0.17	0.08	0.12	0.21	0.01	0.09
18 PE	48.16	4.10	22.16	0.27	0.02	0.20	0.17	0.08	-0.22
19 FM	48.06	4.26	22.56	0.26	0.05	0.13	0.07	0.23	0.18
21 PE	47.94	3.97	22.26	0.16	0.06	0.11	-0.05	-0.06	-0.12
22 PE	47.86	3.91	22.20	0.10	0.46	0.15	-0.13	-0.12	-0.18
25 PE	47.99	4.10	21.75	0.24	0.05	0.10	0.00	0.07	-0.63
26 PE	47.72	4.02	22.47	0.02	0.11	0.42	-0.27	-0.01	0.09
27 FM	47.90	4.05	22.15	0.00	0.30	0.10	0.09	0.02	-0.23
28 PE	47.86	4.06	22.60	0.00	0.04	0.13	-0.13	0.03	0.22
29 FM	47.84	4.04	22.47	0.01	0.06	0.00	-0.15	0.01	0.09
30 PE	48.08	4.00	22.47	0.15	0.23	0.26	0.09	-0.03	0.09
31 FM	48.13	3.94	22.38	0.30	0.19	0.24	0.14	-0.09	0.00
33 FM	48.24	4.64	22.84	1.02	0.48	0.02	0.25	0.64	0.46
34 PE	47.98	4.12	22.82	0.13	0.05	0.23	-0.01	0.09	-0.03

<sup>a</sup> Theoretical % C, 47.99; % H, 4.03; % N, 22.38.

<sup>b</sup> Analyzer used: FM = F&M Scientific Model 185 (Hewlett-Packard); PE = Perkin-Elmer Model 240.

<sup>c</sup> D = difference between duplicate values.

<sup>d</sup> X = deviation of mean from theoretical.

Table 2. Collaborative results for sulfanilamide<sup>a</sup>

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
1 FM	42.00	4.82	16.29	0.09	0.07	0.22	0.15	0.76	0.02
2 FM	41.82	4.76	16.29	0.22	0.23	0.12	-0.03	0.07	0.02
3 PE	41.72	4.52	16.44	0.15	0.13	0.08	-0.13	-0.17	-0.17
4 FM	41.82	4.60	16.32	0.21	0.01	0.08	-0.03	-0.03	0.05
5 PE	41.86	4.70	16.28	0.11	0.09	0.21	0.01	0.01	0.01
6 FM	42.06	4.39	15.86	1.87	0.44	0.20	0.21	-0.30	-0.41
7 FM	41.40	4.69	16.18	0.23	0.04	0.00	-0.45	0.00	-0.09
8 PE	41.40	4.80	16.65	0.10	0.01	0.36	-0.45	0.11	0.38
9 PE	41.71	4.86	16.48	0.14	0.20	0.10	-0.14	0.17	0.21
10 PE	41.96	4.72	16.38	0.21	0.00	0.07	0.11	0.03	0.11
11 PE	41.91	4.70	16.35	0.08	0.02	0.26	0.06	0.01	0.08
12 PE	41.86	4.82	16.41	0.07	0.15	0.04	0.01	0.13	0.14
13 PE	42.12	4.64	16.38	0.17	0.13	0.25	0.27	0.05	0.11
14 FM	41.98	4.64	16.34	0.15	0.07	0.19	0.13	-0.05	0.07
15 FM	41.75	4.66	16.19	0.00	0.05	0.00	-0.10	-0.03	-0.08
15 PE	41.66	4.70	16.29	0.13	0.27	0.06	-0.19	0.01	0.02
16 FM	41.35	4.74	16.12	0.05	0.00	0.05	-0.50	0.05	-0.15
17 PE	41.75	4.68	16.19	0.08	0.03	0.06	-0.10	-0.01	-0.08
18 FM	42.04	4.68	16.23	0.05	0.09	0.24	0.19	0.01	-0.04
19 FM	41.68	4.66	16.37	0.14	0.01	0.30	-0.17	-0.03	0.10
21 PE	41.82	4.69	16.11	0.03	0.06	0.04	-0.03	0.00	-0.16
22 PE	41.54	4.73	16.06	0.03	0.08	0.17	-0.31	0.04	-0.21
25 PE	41.82	4.62	15.84	0.15	0.20	0.07	-0.03	-0.07	-0.43
26 PE	41.63	4.59	16.26	0.12	0.12	0.47	-0.22	-0.10	-0.01
27 FM	41.80	4.50	16.05	0.20	0.20	0.30	-0.05	-0.19	-0.22
28 PE	41.66	4.73	16.34	0.19	0.00	0.13	-0.19	0.04	0.07
29 FM	41.71	4.73	16.32	0.74	0.26	0.33	-0.14	0.04	0.05
30 PE	42.08	4.59	16.29	0.25	0.26	0.02	0.23	-0.10	0.02
31 FM	42.28	4.67	16.14	0.16	0.12	0.01	0.43	-0.02	-0.13
33 FM	41.38	4.70	16.13	0.71	0.21	0.18	-0.47	0.01	-0.14
34 PE	41.94	4.68	16.02	0.16	0.06	0.05	0.11	-0.01	-0.25

**Table 3. Collaborative results for S-benzyl<sup>a</sup>**

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
1 FM	47.54	5.54	13.94	0.24	0.04	0.05	0.14	-0.07	0.12
2 FM	47.30	5.44	13.80	0.10	0.19	0.13	-0.10	-0.03	-0.02
3 PE	47.21	5.42	14.06	0.10	0.12	0.04	-0.19	-0.05	0.24
4 FM	47.39	5.51	13.88	0.30	0.02	0.08	-0.01	0.04	0.06
5 PE	47.32	5.46	13.98	0.21	0.03	0.01	-0.08	-0.01	0.06
6 FM	47.99	5.60	13.76	2.36	1.22	0.25	0.59	0.13	-0.06
7 FM	46.63	5.40	13.74	0.74	0.00	0.05	0.23	-0.07	0.08
8 PE	46.70	5.46	14.22	0.04	0.01	0.03	-0.70	-0.01	1.10
9 PE	47.34	5.52	13.99	0.04	0.11	0.02	-0.06	0.05	0.17
10 PE	47.42	5.51	13.93	0.49	0.04	0.00	0.02	0.04	0.11
11 PE	47.42	5.54	13.92	0.00	0.33	0.01	0.02	0.07	0.10
12 PE	47.45	5.26	13.96	0.10	0.02	0.07	0.05	-0.21	0.10
13 PE	47.42	5.42	13.97	0.04	0.01	0.06	0.02	0.02	0.15
14 FM	47.58	5.48	13.90	0.23	0.20	0.15	0.18	0.01	0.06
15 FM	47.16	5.56	13.69	0.05	0.11	0.22	-0.24	0.09	-0.13
15 PE	47.34	5.50	14.10	0.09	0.12	0.01	-0.06	0.03	0.28
16 FM	46.48	5.46	13.58	0.53	0.03	0.29	-0.92	-0.01	-0.24
17 PE	47.29	5.47	13.96	0.40	0.02	0.24	-0.11	0.00	0.14
18 FM	47.24	5.39	13.82	0.21	0.02	0.09	-0.16	-0.08	0.00
19 FM	47.16	5.68	14.02	0.46	0.61	0.19	-0.24	0.21	0.20
21 PE	47.42	5.40	13.77	0.01	0.14	0.10	0.02	-0.07	-0.05
22 PE	47.16	5.42	13.76	0.27	0.07	0.17	-0.24	-0.05	0.06
25 PE	47.30	5.18	13.56	0.00	0.15	0.03	-0.10	-0.29	-0.26
26 PE	47.22	5.40	13.96	0.19	0.05	0.37	-0.18	-0.07	0.14
27 FM	46.95	5.25	14.0	0.10	0.10	0.00	-0.45	-0.22	0.18
28 PE	47.40	5.68	13.92	0.12	0.09	0.02	-0.07	-0.21	0.10
29 FM	47.34	5.28	13.95	0.05	0.19	0.02	-0.06	-0.19	0.13
30 PE	47.44	5.45	13.87	0.09	0.00	0.04	0.04	-0.02	0.05
31 FM	47.48	5.64	13.80	0.05	0.01	0.04	0.08	0.17	-0.02
33 FM	47.62	5.50	14.06	1.23	0.28	0.27	0.22	0.03	0.24
34 FM	47.63	5.43	13.75	0.10	0.06	0.18	0.23	-0.04	0.07

<sup>a</sup> Theoretical % C, 47.40; % H, 5.47; % N, 13.82.

<sup>b-d</sup> See Table 1.

**Table 4. Collaborative results for nicotinic acid<sup>a</sup>**

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
1 FM	58.52	4.12	11.32	0.17	0.02	0.05	-0.01	0.03	-0.06
2 FM	58.39	4.00	11.39	0.08	0.01	0.04	-0.21	-0.09	0.01
3 PE	58.52	3.89	11.39	0.12	0.02	0.14	-0.01	-0.20	0.01
4 FM	58.56	4.08	11.40	0.00	0.01	0.07	0.03	-0.01	0.02
5 PE	58.59	4.18	11.48	0.36	0.13	0.01	0.06	0.09	0.10
6 FM	60.50	5.08	11.41	4.03	0.43	0.24	1.97	0.99	0.03
7 FM	58.48	4.00	11.48	0.26	0.12	0.05	-0.05	-0.09	0.10
8 PE	57.90	3.94	11.42	0.36	0.11	0.09	-0.63	-0.15	0.04
9 PE	58.28	4.22	11.45	0.19	0.19	0.02	-0.25	0.13	0.07
10 PE	58.60	4.12	11.48	0.17	0.05	0.08	0.07	0.03	0.10
11 PE	58.39	4.05	11.28	0.02	0.02	0.02	-0.14	-0.04	-0.10
12 PE	58.36	4.10	11.40	0.00	0.05	0.07	-0.17	0.01	0.02
13 PE	58.56	4.04	11.52	0.17	0.04	0.01	0.03	-0.05	0.14
14 FM	58.30	4.04	11.46	0.25	0.18	0.15	-0.23	-0.05	-0.08
15 FM	57.76	4.10	11.35	0.04	0.06	0.16	-0.77	0.01	-0.03
15 PE	57.92	3.98	11.21	1.77	0.24	0.08	-0.61	-0.11	-0.17

Table 4. (Continued)

Coll. <sup>b</sup>	Mean %			D <sup>c</sup>			X <sup>d</sup>		
	C	H	N	C	H	N	C	H	N
16 FM	58.18	3.28	11.15	0.12	0.55	0.08	-0.35	-0.81	-0.23
17 PE	58.58	4.04	11.40	0.41	0.08	0.19	0.05	-0.05	0.02
18 FM	58.30	4.02	11.26	0.17	0.13	0.02	-0.23	-0.05	-0.12
19 FM	58.38	3.86	11.30	0.04	0.13	0.09	-0.15	-0.23	-0.08
21 PE	58.34	4.12	11.12	0.18	0.04	0.00	-0.19	0.03	-0.26
22 PE	58.66	3.92	11.32	0.43	0.07	0.07	0.13	-0.17	-0.05
25 PE	58.61	4.26	11.26	0.12	0.05	0.03	0.08	0.17	-0.12
26 PE	58.22	4.10	11.22	0.09	0.12	0.25	-0.31	0.01	-0.16
27 FM	58.70	4.20	10.75	0.04	0.00	0.10	0.17	0.11	-0.63
28 PE	58.60	4.22	11.38	0.17	0.15	0.07	0.07	0.13	0.00
29 FM	58.40	4.01	11.46	0.99	0.06	0.07	-0.13	-0.08	0.08
30 PE	58.74	3.93	11.40	0.03	0.14	0.09	0.21	0.16	0.02
31 FM	59.01	4.00	11.26	0.54	0.07	0.04	0.48	-0.09	-0.12
33 FM	58.34	4.16	11.77	0.47	0.08	0.42	-0.19	0.07	0.39
34 PE	58.89	4.25	11.44	0.26	0.14	0.01	0.07	0.16	-0.06

<sup>a</sup> Theoretical % C, 58.53; % H, 4.09; % N, 11.38.<sup>b-d</sup> See Table 1.Table 5. Collaborative results for stearic acid<sup>a</sup>

Coll. <sup>b</sup>	Mean %		D <sup>c</sup>		X <sup>d</sup>	
	C	H	C	H	C	H
1 FM	75.82	12.72	0.11	0.22	-0.17	-0.05
2 FM	77.09	12.04	0.10	0.16	1.10	-0.73
3 PE	76.20	12.96	0.05	0.15	0.21	0.19
4 FM	77.31	13.36	0.13	0.03	1.32	0.59
5 PE	76.02	12.76	0.19	0.29	0.03	-0.01
6 FM	78.20	12.70	0.35	0.17	2.21	-0.07
7 FM	76.41	12.64	0.06	0.07	0.42	-0.15
8 PE	75.06	12.93	0.26	0.04	-0.93	0.16
9 PE	76.10	13.05	0.19	0.18	0.11	0.28
10 PE	75.92	12.69	0.12	0.08	-0.07	0.08
11 PE	75.96	13.00	0.03	0.07	-0.03	-0.23
12 PE	76.25	13.04	0.08	0.07	-0.43	0.27
13 PE	76.28	12.88	0.25	0.05	0.29	0.11
14 FM	76.12	12.77	0.13	0.26	0.13	0.00
15 PE	75.76	12.74	0.04	0.19	-0.23	-0.03
16 FM	76.88	12.60	1.48	0.79	0.89	0.17
17 PE	75.95	13.22	0.06	0.17	0.04	0.59
18 PE	76.18	12.80	0.21	0.03	0.19	0.03
19 FM	77.54	12.79	0.51	0.34	1.55	0.02
21 PE	76.08	12.78	0.38	0.03	0.09	0.01
22 PE	76.06	12.85	0.55	0.09	0.07	0.08
25 PE	75.90	11.88	0.01	0.15	-0.09	-0.89
26 PE	75.91	12.90	0.02	0.06	-0.08	0.13
27 FM	77.05	12.30	1.90	0.40	1.06	-0.47
28 PE	76.18	12.60	0.21	0.06	0.19	-0.17
29 FM	76.66	12.79	0.36	0.18	0.67	0.02
30 PE	76.54	12.32	0.06	0.28	0.55	-0.45
31 FM	78.00	13.56	0.87	0.79	2.01	0.79
33 FM	77.34	12.34	0.81	0.06	1.35	-0.43
34 FM	76.72	12.80	0.23	0.19	0.73	0.03

<sup>a</sup> Theoretical % C, 75.99; % H, 12.77.<sup>b-d</sup> See Table 1.

**Table 6. Collaborative results for ethyl laurate<sup>a</sup>**

Coll. <sup>b,c</sup>	Mean %		D <sup>c</sup>		X <sup>d</sup>	
	C	H	C	H	C	H
1 FM	73.24	12.35	0.01	0.03	-0.39	-0.01
3 PE	73.76	12.32	0.15	0.19	0.13	-0.04
4 FM	74.05	12.69	0.18	0.20	0.42	0.33
5 PE	73.61	12.32	0.01	0.34	-0.02	-0.04
6 FM	77.05	12.97	2.66	0.14	3.42	0.61
7 FM	74.27	12.19	0.12	0.02	0.64	-0.17
8 PE	73.21	12.08	0.18	0.85	-0.42	-0.28
9 PE	73.91	12.74	0.10	0.19	0.28	0.38
10 PE	73.60	12.47	0.37	0.06	-0.03	0.11
11 PE	73.84	12.45	0.01	0.22	0.21	0.09
12 PE	73.54	12.44	0.09	0.34	-0.09	0.08
13 PE	73.38	12.40	0.12	0.11	-0.25	0.04
14 FM	74.31	12.68	0.46	0.14	0.68	0.32
17 PE	73.76	12.42	0.27	0.35	0.13	0.06
18 PE	73.38	12.18	0.26	0.00	-0.25	-0.18
19 FM	74.18	12.62	0.04	0.15	0.55	0.26
21 PE	73.34	12.35	0.03	0.08	-0.26	-0.01
22 PE	73.22	11.94	0.24	0.15	-0.41	-0.42
26 PE	73.82	12.85	0.08	0.22	0.19	0.49
27 FM	73.90	12.15	0.40	0.30	0.27	-0.21
28 PE	73.61	12.20	0.50	0.10	-0.02	-0.16
29 FM	73.20	12.67	0.11	0.02	-0.43	0.31
30 PE	73.94	12.00	0.03	0.12	0.31	-0.36
31 FM	74.58	12.90	0.65	0.30	0.95	0.54
33 FM	71.66	10.93	2.34	1.62	-1.97	-1.43
34 PE	74.22	12.18	0.15	0.17	0.59	-0.18

Theoretical % C, 73.63; % H, 12.36; mp, 10.7°C; bp, 269°C.

<sup>d</sup> See Table 1.

Collaborators 2 (FM) and 16 (FM) did not submit results.

**Table 7. Carbon: statistical results for the 6 compounds studied**

Compound	Anal. <sup>a</sup>	No. of Coll.	$\sigma$	Calc. F	Crit. F 0.01	Av. Dev. <sup>b</sup>	Bias <sup>c</sup>
Sulfadiazine	Total	31	0.39	5.25	2.31	0.21	-0.012
	FM	13	0.55			0.24	+0.12
	PE	18	0.24			0.19	-0.097
Sulfanilamide	Total	31	0.29	20.25	2.34	0.18	-0.067
	FM	14	0.45			0.23	-0.096
	PE	17	0.10			0.15	-0.048
S-Benzyl	Total	31	0.38	17.76	2.34	0.17	-0.045
	FM	14	0.59			0.29	-0.044
	PE	17	0.14			0.08	-0.045
Nicotinic acid	Total	31	0.60	6.79	2.34	0.27	-0.040
	FM	14	0.86			0.38	-0.066
	PE	17	0.33			0.20	-0.11
Stearic acid	Total	30	0.38	15.47	2.34	0.56	+0.46
	FM	12	0.59			1.06	+1.03
	PE	18	0.15			0.24	+0.076
Ethyl laurate	Total	26	0.53	28.89	2.49	0.53	+0.17
	FM	10	0.86			0.62	+0.004
	PE	16	0.16			0.48	+0.27

<sup>a</sup> FM = F&M Scientific Model 185 (Hewlett-Packard); PE = Perkin-Elmer Model 240.

<sup>b</sup> Average deviation of means from theoretical values, ignoring signs.

<sup>c</sup> Average deviation of means from theoretical values, observing signs.

SCROGGINS: AUTOMATED C-H-N DETERMINATION

figure for many of the FM users, indicating that the usual standards are not satisfactory for this type of material. Tables 10 and 11 illustrate the effect of different parameters and parameter combinations on carbon results for the FM and PE apparatus, respectively. Short combustion times, low combustion temperatures, and high oven temperature differentials have a general tendency to cause poor precision and accuracy with FM apparatus. The data for Collaborators 1 and 18

indicate that integration rather than measurement of peak heights leads to better accuracy and precision.

Figure 1 clearly shows that, for good precision, the temperature differential between the GLC ovens should not exceed 20°C. Although 3 analysts, one using an integrator, obtained reasonable accuracy at combustion temperatures below 1080°C, Fig. 2 indicates that the temperature should be 1080°C or higher.

Table 8. Hydrogen and nitrogen: statistical results for the 6 compounds studied

Compound	Anal. <sup>a</sup>	Av. Dev. <sup>b</sup>		Std. Dev.		Bias <sup>c</sup>	
		H	N	H	N	H	N
Sulfadiazine	Total	0.092	0.18	0.18	0.16	+0.026	+0.047
	FM	0.12	0.16	0.18	0.15	+0.079	-0.0092
	PE	0.072	0.19	0.17	0.17	+0.009	+0.084
Sulfanilamide	Total	0.088	0.13	0.11	0.14	+0.014	-0.036
	FM	0.12	0.12	0.14	0.14	+0.030	-0.080
	PE	0.062	0.14	0.084	0.14	+0.005	-0.0061
S-Benzyl	Total	0.084	0.16	0.19	0.10	-0.024	+0.10
	FM	0.10	0.12	0.29	0.14	+0.0067	+0.045
	PE	0.069	0.18	0.082	0.071	-0.045	+0.14
Nicotinic acid	Total	0.15	0.11	0.11	0.091	-0.0047	-0.033
	FM	0.21	0.15	0.15	0.11	-0.0083	-0.043
	PE	0.099	0.084	0.085	0.074	+0.0028	-0.027
Stearic acid	Total	0.24		0.19		-0.016	
	FM	0.29		0.28		-0.13	
	PE	0.18		0.11		+0.051	
Ethyl laurate	Total	0.27		0.19		+0.028	
	FM	0.34		0.17		+0.023	
	PE	0.24		0.20		+0.065	

<sup>a-c</sup> See Table 7.

Table 9. Reproducibility among analysts for carbon analyses

Coll.	$\sigma^a$	Bias <sup>b</sup>	Av. Dev. of Means (Theor.)	Av. Dev. of Means (Theor.) <sup>c</sup>	Coll.	$\sigma^a$	Bias <sup>b</sup>	Av. Dev. of Means (Theor.)	Av. Dev. of Means (Theor.) <sup>c</sup>
1 FM	0.096	-0.045	0.104	0.078	16 FM	0.53	-0.26	0.61	0.54
2 FM	0.092	+0.13	0.31	0.12	17 PE	0.19	-0.02	0.11	0.12
3 PE	0.077	+0.045	0.16	0.15	18 PE	0.18	+0.037	0.20	0.20
4 FM	0.15	+0.29	0.30	0.02	18 FM	0.11	-0.067	0.19	0.19
5 PE	0.16	+0.023	0.057	0.072	19 FM	0.22	+0.27	0.46	0.16
6 FM	1.77	+1.65	1.65	1.06	21 PE	0.13	-0.075	0.11	0.072
7 FM	0.25	+0.14	0.31	0.20	22 PE	0.23	-0.12	0.22	0.20
8 PE	0.19	-0.60	0.60	0.56	25 PE	0.097	-0.06	-0.06	0.052
9 PE	0.10	-0.15	0.19	0.18	26 PE	0.074	-0.14	0.21	0.24
10 PE	0.20	+0.015	0.052	0.052	27 FM	0.56	+0.18	0.35	0.19
11 PE	0.041	-0.002	0.098	0.088	28 PE	0.18	-0.02	0.11	0.12
12 PE	0.057	+0.028	0.14	0.075	29 FM	0.35	-0.04	0.26	0.12
13 PE	0.13	+0.095	0.18	0.13	30 PE	0.098	+0.22	0.22	0.14
14 FM	0.20	+0.18	0.26	0.19	31 FM	0.35	+0.68	0.68	0.28
15 FM	0.071	-0.28	0.28	0.28	33 FM	0.89	-0.14	0.74	0.28
15 PE	0.56	-0.37	0.37	0.41	34 PE	0.13	+0.29	0.29	0.10

<sup>a</sup> Calculated from difference between duplicates for all 6 samples.

<sup>b</sup> Average deviation of means from theoretical values, observing signs.

<sup>c</sup> Average deviation of means from theoretical values; signs were ignored and results from stearic acid and ethyl laurate were eliminated.

**Table 10. Method parameters and carbon results obtained with F&M Model 185 CHN analyzer**

Coll.	Temp. Diff. of Inner-Outer Oven, °C	Combustion		Av. Dev. of Means (Theor.), % C	$\sigma$ , % C
		Time, sec	Temp., °C		
1 <sup>a</sup>	10	20	1040	0.14	0.096
7	15	55	1120	0.31	0.25
29	15	20	1060	0.26	0.37
4	20	40	1080	0.30	0.15
15	20	55	1010	0.37	0.07
18 <sup>b</sup>	20	20	1120	0.19	0.11
19	20	20	1020	0.46	0.22
31	20	20	1020	0.68	0.35
16	25	52	1060	0.61	0.53
2	30	20	1090	0.31	0.56
33	35	20	1040	0.74	0.89
27	40	50	1050	0.35	0.56
6	50	20	1035	1.65	1.77

<sup>a</sup> Used electronic integrator.

<sup>b</sup> Used on-line computer.

### Conclusions and Recommendation

The study shows the choice and control of effective parameter combinations to be critical. The use of an on-line computer or integrator not only saves time but also widens parameter ranges. When the FM apparatus is used, integration of the detector response (area under the GLC curve) seems to be essential unless the standards used have carbon percentages and combustion characteristics similar to those of the samples. Matching standards and samples is not practical and, of course, not possible if the composition of the sample is unknown. These conclusions are based on the Associate Referee's experience as well as on the data from the study.

The FM apparatus is used most successfully under the following conditions: (1) combustion temperature less than 1080°C and reduction temperature at 500°C; (2) a combustion period in the 20-50 sec range, the 40-50 sec period being

**Table 11. Method parameters and carbon results obtained with Perkin-Elmer Model 240 CHN analyzer**

Coll.	Av. Dev. of Means (Theor.), % C	Addnl Catalyst Used	Digitizer (D), Computer (C), or Integrator (I)	Combustion		Balance Used
				Time (>2.33 min), min	Temp. (>970°C), °C	
10	0.052	Co <sub>3</sub> O <sub>4</sub> Ag <sub>2</sub> WO <sub>4</sub>	D			Mettler M5
5	0.057	Ag <sub>2</sub> WO <sub>4</sub> + AgO Ag <sub>2</sub> WO <sub>4</sub> + MgO	D			Cahn G
25	0.06	WO <sub>3</sub> + CoO	I	4		Cahn G
11	0.098			5.5	1000	Cahn G
17	0.11			2.67	990	Mettler M5
28	0.11			5		Mettler UM7
21	0.11				980	Cahn G
12	0.14	MgO		2.75		Cahn G
3	0.16	Ag <sub>2</sub> WO <sub>4</sub> , MgO, Pt ladle				Cahn G
18	0.18	WO <sub>3</sub> + O <sub>2</sub>	C		1000	Mettler M5
13	0.18					Cahn G
9	0.19		I			Cahn G
26	0.21		I			Mettler M5
22	0.22		I	2.75		Cahn G
30	0.22		C			Sartorius 4125
34	0.29					Mettler M5
15	0.37					Mettler M5
8	0.60					Mettler M5

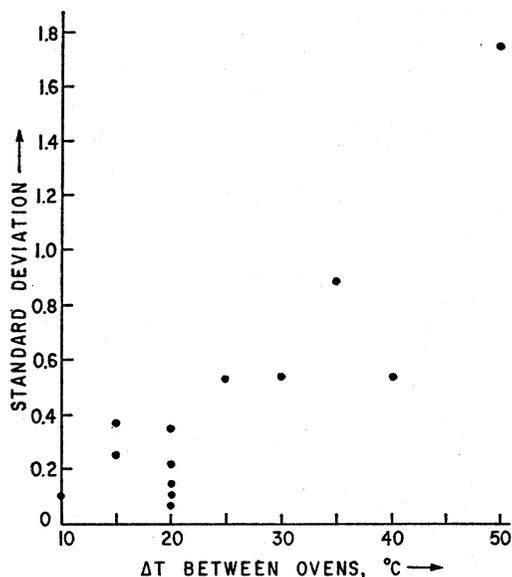


FIG. 1—Plot of temperature difference between ovens vs. standard deviation (F&M apparatus).

preferable for samples difficult to combust; and (3) maintaining the column temperature constant with less than  $\pm 1^\circ\text{C}$  variation by holding the GLC column sub-oven within 5–15°C of the main oven or possibly within 20°C if all other parameters are adequately maintained.

For the best results from the PE apparatus (see Table 11) at least 2 of the following 4 factors should be used: (1) addition to the combustion tube filling of an oxygen-supplying compound or catalyst (such as  $\text{Co}_3\text{O}_4$  and  $\text{Ag}_2\text{WO}_3$ ,  $\text{AgO}$  and  $\text{Ag}_2\text{WO}_3$ , or  $\text{WO}_3$  and  $\text{CoO}$ ); (2) a 3–5 min combustion period; (3) a combustion temperature in the 980–1000°C range and a reduction temperature of about 650°C; and (4) an on-line computer, integrator, or digitizer. The number of collaborators who had difficulty in analyzing ethyl laurate emphasizes the need for caution in the analysis of volatile liquids. The sample should be weighed in capillaries. During the sweeping period the waiting liquid sample must sit in the cooler portion of the combustion tube as near the orifice as possible.

It is recommended that the study of automated procedures for carbon, hydrogen, and nitrogen be continued.

The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee C and was accepted by the Association. See *JAOAC* 54, 392 (1971).

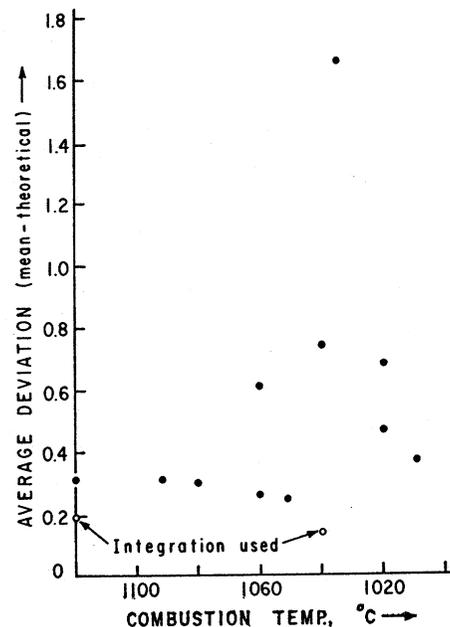


FIG. 2—Plot of combustion temperature vs. average deviation of the means from theoretical values (F&M apparatus).

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