Collaborative Study of the Automatic Carbon, Hydrogen, and Nitrogen Determination

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A method for the simultaneous determination of per cent carbon, hydrogen, and nitrogen, employing automatic instrumentation, was tested by 10 collaborators. The samples analyzed were acetanilide, nicotinic acid, stearic acid, methyl palmitate, and ethyl laurate. Evaluation of the statistical data and overall consideration indicate satisfactory results for all types of compounds studied. The method was adopted as official first action.

In 1970, a collaborative study (Scroggins, L. H. (1971) *JAOAC* **54**, 808–818) was conducted, involving 2 of the most popular types of automatic apparatus for the quantitative microdetermination of carbon, hydrogen, and nitrogen. Evaluation of the collaborative data and overall consideration indicated that satisfactory results could be obtained with either type of instrument, the F&M Model 185 or the Perkin-Elmer Model 240. It was further indicated that definite restrictions on certain parameters should improve the results from both instruments.

In the method presented for study this year, procedural recommendations were based on the data from the 1970 study and emphasis was placed on the type of samples which presented difficulties last year.

METHOD

Carbon, Hydrogen, and Nitrogen Automated Method—Official First Action

42.B01 ***Apparatus***

(a) *Automatic carbon-hydrogen-nitrogen (C-H-N) analyzer.*—Model 185 (FM) (Hewlett-Packard, Rte 41, Avondale, PA 19311), Perkin-Elmer 240 (PE) (Perkin-Elmer Corp.), or equiv.

(b) *Helium.*—Cylinder with pressure regulator and needle valve control. Preheater and purifier optional.

(c) *Oxygen.*—For PE only. Cylinder with pressure regulator and needle valve control.

(d) *Line voltage regulator.*—Optional; 50 amp, output 115 v±0.25%.

(e) *On-line computer or integrator.*—Mandatory for FM app. but optional for PE app.

42.B02 ***Reagents***

(*See* instrument instruction manuals.)

(a) *Catalyst.*—Solid oxidn catalyst (oxides of Co, W, or Ag) required for FM; optional for PE if time and temp. meet conditions specified.

(b) *Std compounds.*—NBS acetanilide, or equiv.

42.B03 ***Preparation of Apparatus***

Prep. and assemble app. as in manual. Adjust preliminary settings and regulate He flow (He and O for PE). Set and let temp. systems equilibrate until constant. Use combustion temp. >1080° for FM and 980–1000° for PE. Use specified 500° and 650° reduction temps, resp., for FM and PE. Maintain detector column suboven within 5–15° of main oven. Adjust bridge current to value specified. After sweeping air "slug" from combustion chamber, use 20–50 sec range combustion period (gas flow diverted) for FM (40–50 sec for samples difficult to burn). Use extended "Hold 30 sec" combustion period for PE. Add Co_3O_4 + Ag_2WO_4, Ag_2O + Ag_2WO_4, or CoO + WO_3 to combustion tube filling of PE. However, if PE is in optimum condition, only 2 of 3 required conditions (temp., time, and catalyst) need be adhered to.

42.B04 ***Determination***

Burn 2 unweighed samples ca 2 mg (PE) or 0.6 mg (FM) to condition app. Make ≥2 blank runs (simulated sample runs without sample) to check and adjust timing of each phase where necessary, to check pattern of final measurements, and to obtain blank factors if required in calcns. Then run std and sample compds, weighed to nearest 0.001 mg or better for PE and 0.0001 mg for FM. Calc. factors as suggested in manual. Rerun std to check factors. Different type std may be used for this rerun. Initially check factors until 2 of 3 detns are within 0.3% of theoretical value. Calc. % C, H, and N, using factors obtained from std compds.

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Special Precautions for Volatile Samples

Weigh volatile samples in capillaries, Al capsules, or Al weighing pans. During sweeping period, volatile samples must be in cooler portion of combustion tube, as near orifice as possible.

Results and Recommendation

Twenty-two collaborators reported carbon, hydrogen, and nitrogen data. The results of 12 collaborators were eliminated on the following bases: (*1*) 5 used an F&M apparatus which did not have an integrator attached to it, and (*2*) 7 did not adhere to the parameters specified in the preliminary setup. The results of the remaining 10 collaborators were analyzed statistically. Six collaborators used as standards acetanilide or cyclohexanone-2,4-dinitrophenylhydrazone or both, 2 used stearic and palmitic acids, and 2 used phenacetin.

Table 1 contains the mean, difference between duplicate values, and deviation of mean from theoretical value for each of the 5 samples.

The statistics in Tables 2 and 3 summarize the data for all 5 compounds. The overall average deviation of the mean from the theoretical value for carbon for all samples analyzed is less than 0.20, for hydrogen less than 0.12, and for nitrogen less than 0.06.

Within-laboratory precision, calculated from the difference between duplicates, bias, and average deviation of the mean from theoretical value, is shown in Table 4. Overall results are improved for the problem compounds when the present modified method is used (Table 5).

Although any 2 of the 3 parameter combinations specified proved satisfactory, results indicated that the order of desirability of the 2 parameter combinations is (*1*) the use of the catalyst filling plus higher combustion temperature, (*2*) catalyst plus the additional "hold 30 sec" combustion time, (*3*) the slightly less successful combination of higher combustion temperature plus the "hold 30 sec" combustion time. During this study, collaborators successfully determined per cent carbon, hydrogen, and nitrogen in ethyl laurate by placing the sample (*1*) in an aluminum capsule wrapped in platinum foil, (*2*) in a capillary placed in a platinum boat, (*3*) in an aluminum sleeve, (*4*) in an aluminum capsule with platinum gauze in the ladle, (*5*) in micropipets, (*6*) in glass ampoules, and (*7*) in quartz capillaries.

The study shows that this method, which has

Table 1. Collaborative results for automated determination of carbon, hydrogen, and nitrogen

	Mean Per Cent			Diff. Betw. Dupls.			Dev. of Mean from Theor.		
Coll.[a]	C	H	N	C	H	N	C	H	N
				Acetanilide[b]					
1 PE	70.94	6.66	10.37	0.19	0.05	0.02	0.15	−0.05	0.0_1
4 FM	71.16	6.67	10.37	0.03	0.08	0.04	0.07	−0.04	0.0_1
8 FM-PE	71.07	6.74	10.37	0.14	0.09	0.06	−0.02	0.03	0.0_4
29 PE	71.16	6.68	10.32	0.05	0.17	0.07	0.07	−0.03	-0.0_6
33 PE	71.18	6.92	10.42	0.08	0.05	0.12	0.09	0.21	0.0_4
34 PE	71.04	6.61	10.32	0.20	0.16	0.07	−0.05	−0.10	-0.0_3
35 PE	71.30	6.75	10.39	0.05	0.06	0.16	0.21	0.04	0.0_2
37 PE	71.04	6.72	10.34	0.31	0.17	0.12	−0.05	0.01	-0.0_4
39 PE	71.08	6.74	10.32	0.20	0.21	0.04	−0.01	0.03	-0.0_2
41 FM	71.16	6.82	10.34	0.09	0.09	0.05	0.07	0.11	−0.0
				Nicotinic Acid[c]					
1 PE	58.34	3.92	11.39	0.14	0.13	0.10	−0.16	−0.17	0.01
4 FM	58.62	4.22	11.33	0.05	0.07	0.00	0.12	0.13	−0.05
8 FM-PE	58.40	4.09	11.44	0.14	0.09	0.06	−0.10	0.00	0.06
29 PE	58.64	4.14	11.44	0.03	0.05	0.19	0.14	0.05	0.06
33 PE	58.61	4.00	11.42	0.18	0.28	0.03	0.11	−0.09	0.04
34 PE	58.65	4.26	11.42	0.16	0.08	0.00	0.15	0.17	0.04
35 PE	58.52	4.02	11.40	0.12	0.02	0.12	0.02	−0.07	0.02
37 PE	58.56	4.04	11.40	0.41	0.08	0.37	0.06	−0.05	−0.02
39 PE	58.52	4.16	11.26	0.16	0.15	0.19	0.02	0.07	−0.12
41 FM	58.46	4.00	11.22	0.03	0.15	0.17	−0.04	−0.09	−0.16

Table 1. *(Continued)*

Coll.[a]	Mean Per Cent			Diff. Betw. Dupls.			Dev. of Mean from Theor.		
	C	H	N	C	H	N	C	H	N
				Stearic Acid[d]					
1 PE	76.16	12.82	—	0.16	0.29	—	0.17	0.05	—
4 FM	75.96	12.75	—	0.07	0.04	—	−0.03	−0.02	—
8 FM-PE	76.06	12.90	—	0.23	0.07	—	0.07	0.13	—
29 PE	76.36	12.67	—	0.04	0.22	—	0.37	−0.10	—
33 PE	76.22	12.86	—	0.06	0.05	—	0.23	0.09	—
34 PE	76.08	12.76	—	0.19	0.25	—	0.09	−0.01	—
35 PE	75.93	12.77	—	0.11	0.02	—	−0.06	0.00	—
37 PE	76.00	12.61	—	0.29	0.26	—	0.01	−0.16	—
39 PE	76.11	12.60	—	0.18	0.01	—	0.12	−0.17	—
41 FM	76.11	12.80	—	0.12	0.01	—	0.12	0.03	—
				Methyl Palmitate[e]					
1 PE	75.64	12.69	—	0.21	0.10	—	0.15	0.02	—
4 FM	75.33	12.80	—	0.06	0.19	—	−0.16	0.13	—
8 FM-PE	75.29	12.80	—	0.00	0.05	—	−0.20	0.13	—
29 PE	75.86	12.66	—	0.07	0.17	—	0.37	−0.01	—
33 PE	75.56	12.63	—	0.13	0.20	—	0.07	−0.04	—
34 PE	75.40	12.95	—	0.26	0.12	—	−0.09	−0.28	—
35 PE	75.34	12.55	—	0.15	0.18	—	−0.15	−0.12	—
37 PE	75.90	12.72	—	0.20	0.47	—	0.41	0.05	—
39 PE	75.40	12.60	—	0.13	0.00	—	−0.09	−0.07	—
41 FM	75.56	12.88	—	0.26	0.17	—	0.07	0.21	—
				Ethyl Laurate[f]					
1 PE	73.74	12.22	—	0.01	0.01	—	0.11	−0.11	—
4 FM	73.24	12.52	—	0.00	0.25	—	−0.39	−0.19	—
8 FM-PE	73.67	12.30	—	0.10	0.04	—	0.04	−0.03	—
29 PE	73.84	12.42	—	0.08	0.20	—	0.21	0.09	—
33 PE	74.26	12.46	—	0.19	0.08	—	0.63	0.13	—
34 PE	73.74	12.52	—	0.45	0.12	—	0.11	0.19	—
35 PE	73.71	12.34	—	0.16	0.01	—	0.08	0.01	—
37 PE	73.70	12.48	—	0.10	0.39	—	0.07	0.15	—
39 PE	73.84	12.36	—	0.01	0.02	—	0.21	0.03	—
FM	73.59	12.54	—	0.04	0.11	—	−0.04	0.21	—

[a] Analyzers used: FM = F & M Scientific Model 185 (Hewlett-Packard); PE = Perkin-Elmer Model 240.
[b] Theoretical per cent C, 71.09; H, 6.71; N, 10.36.
[c] Theoretical per cent C, 58.50; H, 4.09; N, 11.38.
[d] Theoretical per cent C, 75.99; H, 12.77.
[e] Theoretical per cent C, 75.49; H, 12.67.
[f] Theoretical per cent C, 73.63; H, 12.33.

incorporated in it the choice and control of effective parameter combinations indicated by the previous collaborative study, produces satisfactory results. It is recommended that the method be adopted as official first action.

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Table 2. Statistical results for carbon for the 5 compounds studied (10 collaborators)

Sample	Std Dev.	Av. Dev.[a]	Bias[b]
Acetanilide	0.11	0.08	0.023
Nicotinic acid	0.12	0.09	0.032
Stearic acid	0.12	0.13	0.109
Methyl palmitate	0.12	0.18	0.038
Ethyl laurate	0.10	0.19	0.103

[a] Average deviation of means from theoretical values, ignoring signs.
[b] Average deviation of means from theoretical values, observing signs.

Table 3. Statistical results for hydrogen and nitrogen for the 5 compounds studied (10 collaborators)

Sample	H	N
	Av. Dev.[a]	
Acetanilide	0.065	0.028
Nicotinic acid	0.089	0.058
Stearic acid	0.076	
Methyl palmitate	0.106	
Ethyl laurate	0.114	
	Std Dev.	
Acetanilide	0.089	0.050
Nicotinic acid	0.10	0.12
Stearic acid	0.12	
Methyl palmitate	0.14	
Ethyl laurate	0.12	
	Bias[b]	
Acetanilide	0.021	-.004
Nicotinic acid	−0.005	−0.012
Stearic acid	−0.016	
Methyl palmitate	0.002	
Ethyl laurate	0.048	

[a] Average deviation of means from theoretical values, ignoring signs.
[b] Average deviation of means from theoretical values, observing signs.

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Table 4. Reproducibility among analysts for carbon

Coll.	Std Dev.	Av. Dev.[a]
1 PE[b]	0.11	0.15
4 FM	0.03	0.15
8 FM-PE	0.09	0.09
29 PE	0.04	0.23
33 PE	0.10	0.23
34 PE	0.19	0.10
35 PE	0.09	0.10
37 PE	0.20	0.12
39 PE	0.11	0.09
41 FM	0.10	0.07

[a] Average deviation of means from theoretical values, ignoring signs.
[b] Analyzers used: FM = F & M Scientific Model 185 (Hewlett-Packard); PE = Perkin-Elmer Model 240.

Table 5. Comparison of collaborative test results for per cent carbon, 1970 vs. 1971 studies

	Std Dev.		Av. Dev.[a]	
Compound	1970	1971	1970	1971
Nicotinic acid	0.60	0.12	0.27	0.09
Stearic acid	0.38	0.12	0.56	0.13
Ethyl laurate	0.53	0.10	0.53	0.19

[a] Average deviation of means from theoretical values, ignoring signs.

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