INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY
ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON MICROCHEMICAL TECHNIQUES

A STUDY OF THE ACCURACY AND PRECISION OF METHODS FOR THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

Prepared for publication by

M. Večeřa and J. Horská
Institute of Chemical Technology, Pardubice, Czechoslovakia

LONDON
BUTTERWORTHS

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON MICROCHEMICAL TECHNIQUES†

A STUDY OF THE ACCURACY AND PRECISION OF METHODS FOR THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

1. INTRODUCTION

The study was made within the terms of reference of the activities of the Commission on Microchemical Techniques of the International Union of Pure and Applied Chemistry during the period 1962–1965. The objects of the study were as follows. (i) To test various methods for the microdetermination of carbon and hydrogen in organic compounds by analysing selected standard compounds of various compositions. (ii) To estimate the precision of the various determinations in terms of standard deviation and to assess the confidence limits of individual analyses. (iii) To determine whether or not some elements (particularly N, S, I, F, K, P) affect the accuracy and precision of the determination of carbon and hydrogen. (iv) To obtain a survey of the procedures used in routine practice (weighing of samples, combustion method, reagents, methods of final determination, etc.). (v) To obtain a basis for further investigations and developments of methods of organic elemental analysis.

1.1 Standard compounds

Eight substances were chosen from the standard compounds recommended by the Commission on Microchemical Techniques. The compounds were selected so that the following combinations of elements were obtained: (a) C, H; (b) C, H, O; (c) C, H, N, O (nitro compound); (d) C, H, F; (e) C, H, I; (f) C, H, S; (g) C, H, P; (h) C, H, K. The actual compounds are listed in *Table 1*.

Table 1. List of standard compounds analysed

	Compound	*Empirical formula*	*Molecular weight*	C (%)	H (%)
I	Anthracene	$C_{14}H_{10}$	178·234	94·34	5·66
II	Cholesterol	$C_{27}H_{46}O$	386·665	83·87	11·99
III	2,4-Dinitrophenylhydrazine	$C_6H_6N_4O_4$	198·146	36·37	3·05
IV	*o*-Iodobenzoic acid	$C_7H_5IO_2$	248·027	33·90	2·03
V	Sulphanilamide	$C_6H_8N_2O_2S$	172·212	41·85	4·68
VI	*p*-Fluorobenzoic acid	$C_7H_5FO_2$	140·117	60·00	3·60
VII	Triphenylphosphate	$C_{18}H_{15}PO_4$	326·295	66·26	4·63
VIII	Potassium acid phthalate	$C_8H_5KO_4$	204·228	47·05	2·47

---

† *Titular Members:* W. Schöniger, Chairman (Switzerland); R. Lévy, Secretary (France); H. Flaschka (U.S.A.); N. E. Gel'man (U.S.S.R.); O. D. Koch (Germany); W. Koch (Germany); A. Steyermark (U.S.A.); M. Večeřa (Czechoslovakia). *Associate Members:* K. L. Cheng (U.S.A.); J. Körbl (Czechoslovakia); A. M. G. Macdonald (U.K.); H. Malissa (Austria).

1.2 Organization of the study

Compounds I–VIII (40–50 mg of each) were sent to the participants who had previously agreed to cooperate. Four analyses of each compound were required, i.e. a total of 32 determinations. Each participant was asked to give basic information on the method of analysis used. Dr Al Steyermark arranged for the dispatch of samples and the collection of results from laboratories in the U.S.A. Dr Večeřa was in charge of participants from other countries.

1.3 Participants in the study

The names and addresses of the participants are listed in *Table 2.*

1.4 Basic statistical methods used

The standard deviations of the results obtained for each compound by each laboratory were calculated according to the formula:

$$\sigma = \sqrt{\left(\frac{\sum_{i=1}^{m} (x_i - \bar{x})^2}{m - 1}\right)}$$

The standard deviation of the results obtained in l laboratories (where the particular compound was analysed in the same way) was calculated as follows:

$$s^2 = \frac{\sum_{j=1}^{l} \sigma^2}{l} + \frac{\sum_{j=1}^{l} (\bar{x} - \bar{\bar{x}})^2}{l - 1}$$

The variances of the results were compared by means of the Snedecor test (F-test).

The means and the deviations of the means from the true value for each laboratory in which m determinations were made, were calculated in the usual way, i.e.

$$\bar{x} - \mu = \frac{\sum_{j=1}^{m} (\bar{x}_i - \mu)}{m}$$

Similarly, the deviation of the means from the true value for a method used in l laboratories is given by the formula:

$$\bar{\bar{x}} - \mu = \frac{\sum_{j=1}^{l} (\bar{x} - \bar{\bar{x}})}{l}$$

The statistical significance of the difference between the mean and true values was estimated by the Student test

$$t = \frac{\bar{x}}{s_{\bar{x}}} \qquad \text{or} \qquad t = \frac{\bar{\bar{x}}}{s_{\bar{\bar{x}}}}$$

where

$$s_{\bar{x}} = \sqrt{\left(\frac{\sum_{l=1}^{m} (x_i - \bar{x})^2}{m(m - 1)}\right)} \quad \text{and} \quad s_{\bar{\bar{x}}} = \sqrt{\left(\frac{\sum_{j=1}^{l} \sum_{i=1}^{m} (x_{ij} - \bar{\bar{x}})^2}{n(n - 1)}\right)}$$

Table 2. List of participants

Country	*Institute, Company*	*Head of the laboratory*	*Analysts*
Belgium	Gevaert Photo-Producten, Mortsel- Antwerpen	W. Wesenbeek	
	Research Laboratorium Dr. C. Janssen, Beerse	F. Sels	F. Sels
Canada	Analytical Chemistry Research Service, Canada Dept. of Agriculture, Ottawa	D. A. Shearer	G. Moris
Czechoslovakia	Výzkumný ústav organických syntez, Pardubicá -Rybitví	J. Lakomý	J. Lehár
	Výzkumný ústav organických syntez, Pardubice -Rybití.	M. Večeřa	J. Jičínská, H. Šmahelová
Denmark	NOVO Terapeutisk Laboratorium A/S, 115 Fryletakkevej, Copenhagen N.	H. Trutnovsky	L. Sorensen, H. Trutnovsky
France	Centre d'Etudes Nucléares de Saclay	L. Pichat	M. Duvernier
Germany	Mikrochem. Laboratorium der Technischen Universität Dresden	G. Gutbier	H. Zeidler
	Lu -Wittenberg 4, Oskar-Mester-Str.14	L. Seiffarth	Ch. Wroblewski
	Analytisches Laboratorium, Farbenfabrikem Bayer AG., Werk Nerdingen	W. Stuck	W. Hoff
	BASF Untersuchungslaboratorium, Ludwigshafen am Rhein	W. Merz, W. Pfab	
	Farbwerke Hoechst A.G. vormals Meister Lucius & Brüning, Frankfurt (M)	F. Ehrenberger	
Hungary	Institut für Allgemeine Chemie, Technische Universität, Budapest XI, Gellert ter 4.	L. Mázor	K. M. Pápay
India	National Chemical Laboratory, Poona 8	V. S. Pansare	S. J. Rulharui, S. U. Tabib, R. Toteja
Italy	Instituto C. Erba per Ricerce Terapeutiche, Milano	E. Pella	E. Pella, E. Petressi
	Instituto chimico Farmaceutico e Tossicologico dell Universita, Via Taramelli 12, Pavia	A. Campiglio	L. Bozzini, A. Campiglio, F. Preda
Japan	Shionagi Research Laboratory, Shionagi & Co. Ltd., Fukushuma-ku, Osaka	S. Mizukami	Hinako Harama, Hiseko Hasegava, Keiko Noni
Netherlands	Lab. voor organische Scheikunde der Universiteit von Amsterdam, Nieuwe Achtergracht 129.	W. J. Buis	W. J. Buis, H. Pieters
	Statsmijnen in Limburg, Central Laboratory, Geleen	L. Blom	M. Kraus
Switzerland	F. Hoffman-La Roche & Co., Basel	A. Dirscherl	M. Brüger, J. Imhof, G. Nein
	Mikroanalytisches Laboratorium, J.R. Geigy, AG.,	H. Wagner	
	Mikroanalytisches Laboratorium, Sandoz AG., Basel le	W. Schöniger	R. Rudin, P. Saccani, R. Vogt
	Mikroanalytisches Laboratorium der CIBA A.G., Basel	W. Padowetz	B. Karrer, F. Plank, W. Schneider
	Mikrolaboratorium Organ.-chem. Institut Eidg.techn. Hochschule, Zürich	W. Mauser	
	Dr. A. Wander A.G., Bern	H. Lehner	N. Heineman
United Kingdom	Albright & Wilson (Mfg) Ltd., P.O. Box 403, Oldbury, Birmingham	S. Greenfield	R. A. D. Smith
	The University of Liverpool, Department of Organic Chemistry	C. Tomlinson	D. G. Neroman
United States of America	Agricultural Research Service, Albamy, Calif.	L. M. White	G. Secor
	American Cyanamid Co., Bound Brook, N.J.	J. Prokul	
	Chemical Research Division, Army Chemical Centre, Maryland	C. A. Rush	E. J. W. Rhodes

Country	*Institute, Company*	*Head of the laboratory*	*Analysts*
United States of America	Brookhaven National Laboratory, Upton, N.Y.	S. J. Tassinari	D. F. Leahy, S. J. Tassinari
	Coleman Instruments, Inc., 42 Madison Street, Maywood, Ill.	L. Malter	H. Kneuffel
	Special Service Lab., The Dow Chemical Co., Midland, Mich. 48640	S. A. Shrader	
	Du Good Chemical Laboratory, 1215 South Jefferson Street, St. Louis 4, Mo.	L. J. Dinguid	
	du Pont Experimental Station, Wilmington, Del. 19898	V. J. Carrier	V. J. Carrier, J. K. Winter
	E. I. du Pont de Nemours & Co., Wilmington 98, Del. 19898	H. W. Childress	M. A. Spitznagle
	F. & M. Scientific Corp., Avondale, Pa.	O. N. Hinsvark	
	Hoffman-La Roche Inc., Nutley 10, N.J. 07110	A. Steyermark	E. A. Bass, J. C. Dell, J. Kitley, R. Kaup, J. Pao, R. Wetter
	Huffman Microanalytical Laboratories, 3830 High Court, P.O. Box 350 Wheatridge, Colo.	E. W. D. Huffman	
	Chemistry Department, Hunter College, 695 Park Av., New York 21	R. L. Baumgarten	Students
	Lederle Laboratories Division, American Cyanamid Co., Pearl River, N.J.	L. M. Brancone	G. J. Gips, J. J. Ginfrida, S. S. Modes, J. A. Passarello
	The Lilly Research Laboratories, Eli Lilly & Co., Indianopolis 6, Ind. 46206	W. L. Brown	A. C. Brown
	Merck & Co. Inc., Rahway, N.J. 07065	R. N. Boos	F. Antes, L. DeFillipo, J. Marshik, A. Soha
	Micro-Techn. Laboratories, 5044 Warren Avenue, Skolie, Ill.	C. W. Bearley	C. Bearley, J. Gast, M. Nevera, B. Ostrand
	Minnesota Mining & Manufacturing Co., 2301 Hudson Road, St. Paul 19, Minn. 55101	P. B. Olson	R. E. Kolb
	National Bureau of Standards, Washington 25, DC	R. A. Paulson	R. J. Hall, R. A. Paulson
	Norwich Pharmaceutical Co., Norwich, N.J.	G. M. Gustin	G. M. Gustin
	Pennsalt Chemicals Corp., Box 4388, Philadelphia 18, Penn. 19406	H. J. Francis	E. Minnick, R. Smith, O'Brien
	The Procter & Gambel Co., Miami Valley Laboratories, P.O. Box 39175, Cincinnati 39, Ohio 45217	H. W. Wharton	J. L. Waller
	Rohm & Haas Co., Washington Square, Philadelphia 5, Pa.	C. W. Nash	
	Sterling Winthrop Research Inst. Rensselaer, New York 12144	K. D. Fleischer	J. M. Lennon
	University of California, Dept. of Chemistry, Berkeley 4, Cal.	C. W. Koch	F. Balistreri, M. Boisnert, E. Jones, C. W. Koch
	University of Illinois, Dept. of Chemistry, Urbana, Ill.	J. Nemeth	J. D. Callahan, J. Nemeth, M. A. Weatheford
	The Upjohn Company, 301 Henrietta St., Kalamazoo, Mich. 48001	R. C. Anderson	P. A. Spinelli
	Pioneering Research Division, U.S. Army Natick Lab., Natick, Mass.	C. Di Pietro	C. Di Pietro
	USDA, Southern Utilization Research & Development Div. 1100 R. L. Lee Blod, New Orleans, Lo.	A. F. Cucullu	A. F. Cucullu, L. Brown
	Burroughs-Wellcome, Inc., Tuckanoe, N.Y.	S. W. Blackman	P. Giorgio

The statistical significance of the difference of two means was also estimated by the Student test.

$$t_{\mathrm{D}} = (\bar{x}_{\mathrm{A}} - \bar{\bar{x}}_{\mathrm{B}}) \sqrt{\left(\frac{n_{\mathrm{A}} n_{\mathrm{B}} (n_{\mathrm{A}} + n_{\mathrm{B}} - 1)}{(n_{\mathrm{A}} + n_{\mathrm{B}}) \left[\sum_{j=1}^{l_{\mathrm{A}}} \sum_{i=1}^{m_{\mathrm{A}}} (x_{\mathrm{ijA}} - \bar{\bar{x}}_{\mathrm{A}})^2 + \sum_{j=1}^{l_{\mathrm{B}}} \sum_{i=1}^{m_{\mathrm{B}}} (x_{\mathrm{ijB}} - \bar{\bar{x}}_{\mathrm{B}})^2 \right]} \right)}$$

The values calculated for t and F were compared with tabulated values using confidence level 0·05 (95 per cent). The symbols used above are defined as follows:

σ	Standard deviation for each compound in each laboratory
s	Standard deviation for each compound using results from l laboratories
m	Number of determinations done on a particular compound in one laboratory
l	Number of laboratories considered
n	Total number of determinations on one compound in l laboratories
x_i	Result of a single determination for a particular compound in one laboratory
$\bar{x}$	Mean result obtained for a particular compound in one laboratory
$\bar{\bar{x}}$	Mean result obtained for a particular compound in l laboratories
μ	True value
$s_{\bar{x}}, s_{\bar{\bar{x}}}$	Standard deviation of the mean.

2. RESULTS AND DISCUSSION

2.1 Results from individual laboratories

The data calculated from the results obtained for the determination of carbon and hydrogen are given in *Tables 3* and *4*. These data include all the compounds tested and all the collaborating laboratories. In the Tables are given the number of determinations, the deviations of the mean from the true value, the result of the t-test for this deviation, and the standard deviation. The technique used for the final determination is also indicated.

Table 3. Determination of carbon—survey of the results found for individual compounds

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination after combustion*
1	I	4	+0·14	2·800	0·10	COND
	II	4	+0·09	1·636	0·11	
	III	4	+0·05	2·128	0·05	
	IV	4	−0·11	2·750	0·08	
	V	4	+0·11	73·330	0·00	
	VI	4	+0·09	1·241	0·15	
	VII	4	+0·19	8·444	0·06	
	VIII	4	+0·02	0·421	0·10	

Table 3 continued; to be concluded on p. 59

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination after combustion*
1	I	4	−0·14	0·940	0·30	COND ultramicro method
	II	4	0·00	0·000	0·27	
	III	4	+0·19	3·166	0·12	
	IV	4	−0·07	0·848	0·17	
	V	4	+0·15	1·863	0·16	
	VI	4	+0·02	0·182	0·22	
	VII	4	+0·08	0·083	0·19	
	VIII	4	+0·16	1·454	0·22	
2	I	4	+0·02	0·267	0·15	GR
	II	4	+0·02	0·213	0·19	
	III	4	−0·05	0·495	0·20	
	IV	4	−0·03	0·261	0·23	
	V	4	+0·14	1·656	0·17	
	VI	4	+0·12	1·382	0·17	
	VII	4	−0·04	0·477	0·17	
	VIII	4	+0·19	3·512	0·11	
3	I	6	+0·01	0·502	0·05	GR
	II	4	−0·28	5·839	0·10	
	III	4	+0·04	0·518	0·15	
	IV	5	−0·85	11·913	0·16	
	V	5	+0·03	0·360	0·19	
	VI	5	−0·14	1·867	0·17	
	VII	6	+0·20	3·676	0·13	
4	I	7	+0·14	1·351	0·27	GR
	II	7	−0·55	4·505	0·32	
	III	7	−0·10	0·768	0·34	
	IV	5	+0·07	0·338	0·46	
	V	7	+0·12	0·983	0·32	
	VI	4	−0·04	0·267	0·29	
	VII	5	+0·11	0·761	0·32	
	VIII	5	−0·12	0·614	0·44	
5	I	4	−0·06	1·765	0·07	COND
	II	4	+0·02	0·234	0·17	
	III	4	+0·01	0·540	0·04	
	IV	4	−0·03	0·876	0·07	
	V	4	+0·02	0·442	0·09	
	VI	4	−0·06	1·053	0·11	
	VII	4	+0·12	1·809	0·13	
	VIII	4	−0·06	1·770	0·07	
6	I	4	+0·03	0·395	0·15	GR
	II	4	−0·02	0·306	0·13	
	III	4	−0·04	0·729	0·11	
	IV	4	+0·17	6·530	0·05	
	V	4	+0·05	1·887	0·05	
	VI	4	−0·06	0·758	0·16	
	VII	4	−0·09	4·030	0·04	
	VIII	4	+0·08	0·886	0·18	
7	I	4	−0·01	0·151	0·13	GR
	II	4	−0·10	0·474	0·42	
	III	4	0·00	0·000	0·17	
	IV	4	+0·07	1·037	0·13	
	V	4	+0·13	3·125	0·08	
	VI	4	+0·06	1·308	0·09	
	VII	4	−0·08	2·525	0·06	
	VIII	4	+0·14	8·860	0·03	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination after combustion*
8	I	4	−0·19	1·398	0·27	GR
	III	4	+0·48	7·002	0·14	
	IV	4	+0·04	0·487	0·16	
	V	4	−0·53	4·152	0·26	
	VI	4	−0·07	1·823	0·08	
	VII	4	+0·03	0·447	0·13	
	VIII	4	−0·02	0·359	0·11	
9	I	4	0·00	0·000	0·11	TITR
	II	4	−0·33	0·458	0·14	
	III	4	−0·13	4·906	0·05	
	IV	4	+0·03	0·789	0·08	
	V	4	+0·08	1·368	0·12	
	VI	4	+0·08	1·739	0·09	
	VII	4	+0·07	1·842	0·08	
	VIII	4	+0·07	1·609	0·09	
10	I	4	−0·09	1·915	0·09	GR
	II	4	−0·11	2·895	0·08	
	III	4	+0·01	0·208	0·10	
	IV	4	+0·06	0·686	0·18	
	V	3	+0·19	0·229	0·15	
	VI	4	+0·17	3·036	0·11	
	VII	4	+0·31	9·255	0·07	
	VIII	4	+0·40	5·839	0·14	
11	I	4	−0·29	3·140	0·19	GR
	II	4	+1·14	23·265	0·10	
	III	4	+0·23	6·319	0·08	
	IV	4	+0·63	48·837	0·03	
	V	5	+0·45	10·574	0·09	
	VII	5	+0·61	3·416	0·40	
	VIII	7	−1·64	3·675	1·18	
12	I	4	−0·04	1·429	0·06	GR
	II	4	−0·04	1·455	0·06	
	III	4	+0·02	1·379	0·03	
	IV	4	−0·02	0·459	0·09	
	V	4	+0·03	0·600	0·10	
	VIII	4	−0·01	0·488	0·04	
13	I	4	+0·02	0·297	0·13	GR
	II	4	+0·09	1·846	0·10	
	III	4	−0·02	0·496	0·08	
	IV	4	+0·10	3·590	0·06	
	V	4	+0·06	2·400	0·05	
	VI	4	+0·01	0·116	0·17	
	VII	4	+0·21	2·067	0·20	
	VIII	4	+0·03	0·667	0·09	
14	I	4	+0·22	2·543	0·02	GR
	II	4	+0·26	2·706	0·19	
	III	4	+0·21	4·880	0·09	
	IV	4	+0·30	6·662	0·09	
	V	4	+0·23	7·099	0·06	
	VI	4	+0·35	6·469	0·11	
	VII	4	+0·24	3·200	0·15	
	VIII	4	+0·18	20·809	0·02	
15	III	4	+0·11	1·139	0·19	GR
	V	4	+0·05	0·949	0·11	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination after combustion*
16	I	4	+0·12	2·020	0·12	GR
	II	4	−0·30	5·597	0·11	
	III	4	+0·29	2·192	0·26	
	IV	4	+0·94	9·558	0·20	
	V	4	+0·80	0·855	0·19	
	VI	4	−0·33	2·436	0·27	
	VII	4	+0·27	2·423	0·22	
	VIII	4	+0·65	6·002	0·22	
17	I	4	−0·15	1·515	0·20	GR
	II	4	+0·45	4·615	0·20	
	III	4	+0·42	6·885	0·12	
	IV	4	+0·29	3·473	0·17	
	V	4	+0·40	7·339	0·11	
	VI	4	−0·33	8·049	0·08	
	VII	4	+0·47	8·785	0·11	
	VIII	4	+0·20	12·903	0·03	
18	I	4	+0·09	0·079	0·23	GR
	II	4	+0·26	1·659	0·31	
	III	4	+0·30	5·146	0·12	
	IV	4	+0·03	0·194	0·31	
	V	4	+0·12	1·987	0·12	
	VI	4	+0·28	2·038	0·27	
	VII	4	−0·13	1·447	0·18	
	VIII	4	+0·24	3·498	0·14	
19	I	4	+0·13	2·430	0·11	GR
	II	4	−0·36	9·351	0·08	
	III	4	+0·40	9·090	0·08	
	IV	4	+0·29	5·043	0·12	
	V	4	−0·10	1·961	0·10	
	VI	4	+0·22	2·839	0·16	
	VII	4	+0·17	2·297	0·15	
	VIII	4	+0·28	10·980	0·05	
20	I	4	+0·11	2·576	0·09	GR
	II	4	+0·08	0·159	0·10	
	III	4	−0·05	2·083	0·05	
	IV	4	+0·13	2·653	0·10	
	V	4	−0·13	3·062	0·09	
	VI	4	−0·03	0·739	0·08	
	VII	4	−0·14	6·422	0·05	
	VIII	4	−0·15	3·464	0·09	
21	I	4	−0·03	0·273	0·22	COND
	II	4	+0·34	6·233	0·10	
	III	4	+0·06	0·945	0·13	
	IV	4	+0·20	2·249	0·18	
	V	4	−0·01	0·172	0·12	
	VI	4	+0·08	1·553	0·10	
	VII	4	+0·07	0·902	0·16	
	VIII	4	+0·33	7·285	0·09	
22	I	4	+0·12	2·308	0·10	GR
	II	5	+0·05	0·073	0·15	
	III	4	+0·20	26·666	0·02	
	IV	4	+0·19	2·021	0·19	
	V	4	+0·24	4·800	0·10	
	VI	4	+0·19	2·390	0·16	
	VII	5	+0·08	7·435	0·02	
	VIII	4	+0·27	4·737	0·11	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination after combustion*
23	I	4	+0·04	1·572	0·05	GR
	II	4	0·00	0·000	0·08	
	III	4	+0·09	3·232	0·06	
	IV	4	+0·09	2·182	0·08	
	V	4	+0·16	4·233	0·08	
	VI	4	+0·02	0·539	0·07	
	VII	4	+0·05	0·752	0·13	
	VIII	4	+0·12	16·990	0·01	
24	I	2	0·00	0·000	0·06	GR
	II	2	−0·13	2·229	0·06	
	III	2	0·00	0·000	0·01	
	IV	2	+0·42	14·860	0·03	
	V	2	+0·03	0·708	0·04	
	VI	2	−0·06	4·255	0·01	
	VII	2	0·00	0·000	0·10	
	VIII	1	−0·07			
25	I	4	+0·03	0·739	0·08	GR
	II	4	−0·10	1·658	0·12	
	III	4	+0·26	8·553	0·06	
	IV	4	−0·14	1·608	0·17	
	V	4	+0·08	1·242	0·13	
	VI	4	+0·10	2·107	0·09	
	VII	4	+0·02	0·525	0·08	
	VIII	4	−0·01	0·177	0·11	
26	I	6	+0·01	0·064	0·39	GR
	II	6	−0·61	3·967	0·38	
	III	6	−0·09	0·692	0·32	
	IV	6	0·00	0·000	0·40	
	V	6	+0·01	0·095	0·23	
	VI	6	+0·15	1·517	0·22	
	VII	6	−0·15	2·035	0·16	
	VIII	6	−0·29	2·258	0·29	
27	I	4	−0·02	0·228	0·18	GR
	II	4	+0·04	0·361	0·22	
	III	4	+0·10	1·122	0·18	
	IV	4	+0·05	2·674	0·04	
	V	4	+0·05	0·5097	0·20	
	VI	4	−0·03	0·264	0·23	
	VII	4	+0·21	4·918	0·09	
	VIII	4	+0·19	1·916	0·18	
28	I	4	−0·13	0·850	0·31	GR
	II	4	−0·27	2·045	0·26	
	III	4	−0·12	2·162	0·11	
	IV	4	+0·16	2·667	0·12	
	V	4	+0·27	7·105	0·08	
	VI	4	+0·06	1·111	0·11	
	VII	4	−0·05	0·450	0·22	
	VIII	4	+0·07	0·993	0·14	
29	Determinations were done by students and therefore not taken for the calculations					

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination after combustion*
30	I	4	−0·15	4·550	0·07	
	II	4	+0·13	2·630	0·10	
	III	4	+0·06	0·945	0·13	
	IV	4	+0·06	1·579	0·08	GR
	V	4	+0·10	1·563	0·13	
	VI	4	+0·13	2·063	0·13	
	VII	4	+0·22	16·296	0·03	
	VIII	4	+0·20	7·547	0·05	
31	I	4	+0·39	3·450	0·23	
	II	4	−0·04	2·290	0·04	
	III	4	+0·04	0·635	0·13	
	IV	4	+0·22	6·197	0·07	GR
	V	4	+0·19	3·040	0·13	
	VI	4	+0·09	1·956	0·09	
	VII	4	+0·58	4·936	0·24	
	VIII	4	+0·03	0·288	0·21	
32	I	4	−0·02	0·323	0·12	
	II	4	−0·18	2·951	0·12	
	III	4	+0·36	5·806	0·13	
	IV	4	+0·28	7·677	0·07	GR
	V	4	+0·11	2·075	0·11	
	VI	4	+0·02	0·187	0·21	
	VII	4	+0·01	0·282	0·07	
	VIII	4	+0·17	1·473	0·23	
33	I	4	+0·05	0·488	0·21	
	II	4	+0·09	0·340	0·53	
	III	4	+0·13	9·630	0·03	
	IV	5	−0·29	1·758	0·33	GR
	V	4	+0·17	1·675	0·20	
	VI	4	+0·31	3·054	0·20	
	VII	4	−0·04	0·246	0·33	
	VIII	4	+0·21	7·054	0·91	
34	I	4	−0·15	4·411	0·07	
	II	4	+0·07	1·138	0·12	
	III	4	+0·15	1·987	0·15	
	IV	4	+0·06	0·622	0·19	GR
	V	4	+0·14	5·091	0·06	
	VI	4	−0·05	0·680	0·15	
	VII	4	−0·05	19·200	0·03	
	VIII	4	+0·13	1·898	0·14	
35	I	4	+0·06	1·000	0·12	
	II	4	−0·12	1·008	0·24	
	III	4	+0·09	2·466	0·07	
	IV	4	+0·15	2·679	0·11	GR
	V	4	+0·09	1·315	0·14	
	VI	4	+0·10	1·379	0·15	
	VII	4	−0·32	5·664	0·11	
	VIII	4	+0·14	1·172	0·24	
36	I	4	−0·06	0·863	0·14	
	II	4	−0·10	0·172	0·12	
	III	4	+0·13	2·000	0·13	
	IV	4	+0·17	5·484	0·06	GR
	V	4	+0·06	0·822	0·15	
	VI	4	+0·16	4·051	0·08	
	VII	4	−0·18	2·687	0·13	
	VIII	4	+0·05	1·724	0·06	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination after combustion*
37	I	4	+0·04	0·851	0·10	GR
	II	5	+0·10	0·304	0·73	
	III	4	+0·10	6·897	0·03	
	IV	4	−0·03	1·818	0·03	
	V	4	+0·15	7·142	0·04	
	VI	5	−0·59	16·253	0·08	
	VII	4	+0·12	1·875	0·13	
	VIII	6	+0·24	9·375	0·06	
38	I	4	+0·04	0·476	0·17	GR
	II	4	−0·16	1·633	0·20	
	III	4	−0·14	3·182	0·09	
	IV	4	−0·23	3·151	0·15	
	V	4	+0·06	1·765	0·07	
	VI	4	+0·06	3·529	0·03	
	VII	4	−0·16	2·051	0·16	
	VIII	4	−0·07	2·741	0·05	
39	I	4	−0·05	1·887	0·03	GR
	II	4	−0·27	1·543	0·18	
	III	4	−0·04	0·714	0·06	
	V	4	−0·49	3·213	0·15	
40	I	4	+0·12	1·348	0·18	GR
	II	4	+0·11	1·375	0·16	
	III	4	+0·10	1·087	0·18	
	IV	4	−0·11	2·933	0·08	
	V	4	−0·03	0·398	0·16	
	VI	4	+0·10	1·587	0·13	
	VII	4	−0·55	7·051	0·16	
	VIII	4	−0·02	0·158	0·25	
41	I	4	+0·04	2·286	0·04	GR
	II	4	−0·02	0·901	0·04	
	III	4	−0·01	0·178	0·11	
	IV	4	+0·04	1·482	0·05	
	V	4	+0·10	1·639	0·12	
	VI	4	+0·04	3·636	0·02	
	VII	4	+0·03	0·513	0·12	
	VIII	4	+0·11	2·472	0·09	
42	I	4	+0·02	0·471	0·09	GR
	II	4	+0·02	0·421	0·10	
	III	4	+0·09	4·390	0·04	
	IV	4	−0·05	1·266	0·08	
	V	4	+0·09	2·857	0·06	
	VII	4	+0·09	3·103	0·06	
	VIII	4	+0·04	1·290	0·06	
43	I	4	−0·04	0·370	0·22	GLC
	II	3	−0·06	0·647	0·17	
	III	3	+0·16	2·920	0·10	
	IV	3	−0·14	1·264	0·19	
	V	3	+0·19	2·675	0·12	
	VI	3	−0·12	0·880	0·24	
	VII	3	+0·31	2·123	0·25	
	VIII	3	+0·05	0·525	0·17	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination after combustion*
44	I	4	+0·02	0·315	0·13	GR
	II	4	+0·05	0·565	0·18	
	III	4	+0·24	3·779	0·13	
	IV	4	+0·30	4·545	0·13	
	V	4	+0·17	2·267	0·14	
	VI	4	+0·14	6·087	0·05	
	VII	4	+0·15ž	1·500	0·20	
	VIII	4	+0·35	4·375	0·19	
45	II	4	−0·06	1·065	0·11	M
	III	4	0·00	0·000	0·05	
	VII	4	+0·03	0·952	0·06	
46	I	4	−0·03	0·503	0·12	GR
	II	4	+0·09	2·250	0·08	
	III	4	+0·17	6·939	0·05	
	IV	4	+0·10	5·540	0·04	
	V	4	+0·11	3·354	0·07	
	VI	4	+0·01	0·371	0·05	
	VII	4	+0·05	0·671	0·15	
	VIII	4	+0·12	3·023	0·08	
47	I	4	−0·30	2·399	0·25	GR
	III	4	+0·02	3·340	0·12	
	V	4	−0·02	0·055	0·07	
	VII	4	−0·01	1·419	0·14	
48	I	4	−0·24	2·844	0·17	GR
	II	4	−0·04	0·308	0·26	
	III	4	+0·01	0·196	0·10	
	V	4	−0·15	3·061	0·10	
	VI	4	+0·03	0·455	0·13	
	VII	4	+0·26	3·059	0·17	
49	I	4	−0·03	0·198	0·30	GR
	III	4	−0·14	1·701	0·16	
	IV	4	+0·03	0·503	0·12	
	V	4	+0·15	2·230	0·13	
	VI	4	−0·01	0·066	0·30	
	VII	4	0·00	0·000	0·10	
	VIII	4	0·00	0·000	0·29	
50	I	4	−0·09	1·579	0·11	GR
	II	5	−0·30	4·630	0·15	
	III	4	+0·14	11·765	0·02	
	IV	4	+1·99	7·796	0·51	
	V	4	+0·19	8·085	0·05	
	VI	4	−0·05	0·700	0·14	
	VIII	4	+0·08	1·912	0·08	
51	I	4	+0·01	0·166	0·12	GR
	II	4	+0·02	0·429	0·09	
	III	4	+0·01	0·213	0·09	
	IV	4	+0·03	3·000	0·02	
	V	4	−0·06	2·027	0·06	
	VI	4	+0·06	1·899	0·06	
	VII	4	−0·02	0·816	0·05	
	VIII	4	0·00	0·000	0·01	

Table 3—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final aetermination after combustion*
52	I	3	+0·05	1·066	0·08	GR
	II	3	−0·04	1·242	0·06	
	III	2	+0·11	7·801	0·01	
	IV	2	+0·10	7·092	0·01	
	V	3	+0·09	4·319	0·04	
	VI	2	+0·07	0·8139	0·09	
	VII	3	+0·04	1·089	0·08	
	VIII	2	+0·02	1·418	0·01	
53	I	4	+0·07	1·311	0·11	GR
	II	4	+0·06	1·359	0·09	
	III	3	−0·04	0·703	0·10	
	IV	3	−0·81	31·392	0·05	
	VI	4	+0·07	1·132	0·04	
	VI	2	−0·04	0·800	0·05	
	VII	4	+0·04	0·186	0·10	
	VIII	3	+0·04	0·572	0·12	
54	I	4	+0·19	6·822	0·06	GR
	II	4	−0·08	1·163	0·14	
	III	4	+0·11	2·136	0·10	
	IV	4	−0·12	2·791	0·11	
	V	4	+1·26	33·962	0·07	
	VI	4	+0·12	2·791	0·09	
	VII	4	+0·07	4·062	0·08	
	VIII	4	−0·09	1·033	0·17	
55	I	4	−0·05	1·856	0·05	GR
	II	4	−0·09	7·347	0·02	
	III	4	0·00	0·000	0·01	
	V	3	+0·01	17·300	0·01	
	VIII	4	+0·03	1·807	0·03	
56	I	4	+0·22	2·788	0·16	GR
	II	4	−0·13	5·963	0·04	
	III	4	−0·12	1·563	0·15	
	IV	3	+0·20	1·641	0·21	
	V	4	+0·16	1·526	0·21	
	VI	4	+0·05	3·770	0·03	
	VII	4	+0·20	1·952	0·21	
	VIII	4	+0·09	2·541	0·07	
57	I	4	0·00	0·000	0·07	GR
	II	4	−0·01	0·343	0·06	
	III	4	+0·06	1·464	0·08	
	IV	4	+0·11	1·560	0·14	
	V	4	+0·10	4·000	0·05	
	VI	4	+0·08	5·031	0·03	
	VII	4	+0·05	1·114	0·09	
	VIII	4	+0·09	2·195	0·08	

GR gravimetric methods GLC methods with gas chromatography finish COND conductometric methods
M manometric methods TITR titrimetric methods

Table 4. Determination of hydrogen—survey of the results found for individual compound

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination of the combustion product*
1	I	4	+0·02	0·869	0·05	COND
	II	4	−0·06	3·243	0·04	
	III	4	−0·01	0·556	0·04	
	IV	4	+0·03	1·395	0·04	
	V	4	+0·03	22·143	0·03	
	VI	4	+0·08	2·860	0·01	
	VII	4	+0·03	6·000	0·01	
	VIII	4	−0·01	0·769	0·03	
1	I	4	−0·01	0·070	0·03	COND ultramicro method
	II	4	−0·04	0·762	0·10	
	III	4	+0·02	1·081	0·04	
	IV	4	+0·02	1·666	0·02	
	V	4	+0·04	2·580	0·03	
	VI	4	+0·06	4·800	0·03	
	VII	4	+0·02	1·666	0·02	
	VIII	4	−0·03	2·727	0·02	
2	I	4	−0·04	0·435	0·18	GR
	II	4	−0·16	1·592	0·20	
	III	4	+0·10	2·976	0·07	
	IV	4	−0·05	0·840	0·12	
	V	4	+0·06	1·026	0·12	
	VI	4	−0·07	1·354	0·10	
	VII	4	+0·02	0·340	0·12	
	VIII	4	+0·14	1·622	0·17	
3	I	6	+0·03	2·190	0·04	GR
	II	4	−0·20	5·763	0·07	
	III	4	+0·10	2·051	0·10	
	IV	5	+0·04	2·577	0·03	
	V	5	+0·14	5·512	0·06	
	VI	5	+0·13	2·802	0·10	
	VII	6	+0·07	2·243	0·08	
	VIII	4	+0·22	3·554	0·12	
4	I	7	−0·03	0·794	0·09	GR
	II	7	+0·02	0·356	0·15	
	III	7	+0·11	3·380	0·09	
	IV	5	+0·06	2·300	0·02	
	V	7	+0·11	2·921	0·07	
	VI	4	+0·19	5·200	0·07	
	VII	5	+0·23	2·961	0·15	
	VIII	4	+0·18	3·298	0·11	
6	I	4	0·00	0·000	0·06	GR
	II	4	+0·01	0·099	0·20	
	III	4	0·00	0·000	0·17	
	IV	4	+0·12	2·419	0·10	
	V	4	+0·01	0·205	0·10	
	VI	4	+0·22	3·640	0·12	
	VII	4	+0·72	10·510	0·14	
	VIII	4	+0·10	1·448	0·14	

Table 4 continued; to be concluded on p. 67

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination of the combustion product*
7	I	4	−0·02	0·854	0·05	GR
	II	4	−0·08	2·070	0·08	
	III	4	+0·09	1·650	0·04	
	IV	4	+0·00	0·000	0·04	
	V	4	+0·15	5·101	0·06	
	VI	4	−0·06	2·451	0·05	
	VII	4	−0·03	0·839	0·07	
	VIII	4	+0·02	1·332	0·03	
8	I	4	+0·17	2·039	0·17	GR
	III	4	+0·45	8·182	0·11	
	IV	4	+0·18	3·358	0·11	
	V	4	+0·26	5·174	0·10	
	VI	4	+0·11	2·965	0·07	
	VII	4	+0·19	5·121	0·07	
	VIII	4	+0·12	0·790	0·09	
9	I	4	−0·12	10·000	0·02	TITR
	II	4	−0·40	6·838	0·12	
	III	4	+0·04	1·429	0·06	
	IV	4	+0·01	0·606	0·03	
	V	4	+0·01	0·476	0·04	
	VI	4	−0·01	0·364	0·06	
	VII	4	−0·02	1·818	0·02	
	VIII	4	+0·01	0·769	0·03	
10	I	4	+0·06	3·750	0·03	GR
	II	4	+0·05	1·754	0·06	
	III	4	+0·23	13·939	0·03	
	IV	4	+0·08	2·078	0·08	
	V	3	+0·20	4·950	0·07	
	VI	4	−0·05	1·010	0·10	
	VII	4	−0·05	1·333	0·08	
	VIII	4	−0·06	3·158	0·04	
11	I	4	+0·39	4·134	0·19	GR
	II	4	+0·05	1·416	0·07	
	III	4	+0·05	0·861	0·12	
	IV	4	+0·21	8·750	0·05	
	V	4	+1·26	6·438	0·44	
	VII	5	+0·01	0·145	0·15	
	VIII	7	+0·25	3·679	0·18	
12	I	4	+0·01	0·800	0·03	GR
	II	4	+0·01	0·408	0·05	
	III	4	+0·01	0·377	0·05	
	IV	4	−0·01	0·488	0·04	
	V	4	+0·02	0·784	0·05	
	VIII	4	0·00	0·000	0·04	
13	I	4	+0·04	4·624	0·02	GR
	II	4	+0·03	1·415	0·04	
	III	4	+0·10	6·329	0·03	
	IV	4	−0·01	0·365	0·05	
	V	4	+0·03	2·449	0·02	
	VI	4	+0·04	0·702	0·11	
	VII	4	−0·03	0·857	0·07	
	VIII	4	+0·08	4·624	0·03	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$		s	*Method of final determination of the combustion product*
14	I	4	+0·11	4·015	0·05	GR
	II	4	+0·11	27·160	0·01	
	III	4	+0·25	9·615	0·05	
	IV	4	+0·10	6·666	0·03	
	V	4	+0·26	8·025	0·06	
	VI	4	+0·24	7·154	0·07	
	VII	4	+0·09	138·46	0·00	
	VIII	4	+0·05	2·77	0·04	
15	III	4	+0·04	0·560	0·14	GR
	V	4	+0·19	4·000	0·09	
16	I	4	−0·02	0·571	0·07	GR
	II	4	+0·04	0·537	0·15	
	III	4	+0·57	9·306	0·12	
	IV	4	+0·31	8·516	0·07	
	V	4	+0·22	0·414	0·11	
	VI	4	−0·10	1·753	0·12	
	VII	4	−0·01	0·122	0·16	
	VIII	4	+0·19	6·090	0·06	
17	I	4	+0·39	2·806	0·28	GR
	II	4	+0·27	5·714	0·08	
	III	4	+1·37	1·085	0·19	
	IV	4	+0·43	11·944	0·07	
	V	4	+0·48	14·117	0·07	
	VI	4	+0·20	14·286	0·03	
	VII	4	+0·33	6·947	0·10	
	VIII	4	+0·32	10·492	0·06	
18	I	4	+0·11	0·931	0·24	GR
	II	4	−0·24	1·949	0·35	
	III	4	+0·20	4·963	0·08	
	IV	4	+0·17	2·297	0·15	
	V	4	+0·04	0·332	0·24	
	VI	4	+0·14	2·482	0·11	
	VII	4	−0·05	0·446	0·22	
	VIII	4	+0·23	2·669	0·17	
19	I	4	+0·03	0·588	0·10	GR
	II	4	−0·05	1·786	0·06	
	III	4	+0·27	6·506	0·08	
	IV	4	+0·11	0·216	0·10	
	V	4	+0·21	3·684	0·11	
	VI	4	+0·06	2·353	0·05	
	VII	4	+0·18	2·836	0·13	
	VIII	4	+0·03	0·469	0·13	
20	I	4	−0·16	5·06	0·06	M
	II	4	−0·04	0·993	0·08	
	III	4	+0·07	1·537	0·09	
	IV	4	+0·28	3·899	0·14	
	V	4	+0·16	3·624	0·09	
	VI	4	+0·12	2·771	0·09	
	VII	4	+0·07	0·749	0·19	
	VIII	4	+0·05	0·690	0·14	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination of the combustion product*
22	I	4	+0·03	0·400	0·08	GR
	II	5	−0·01	0·018	0·56	
	III	4	+0·11	2·588	0·09	
	IV	4	+0·06	0·960	0·13	
	V	4	−0·09	1·856	0·10	
	VI	4	+0·14	5·833	0·05	
	VII	5	+0·02	0·551	0·08	
	VIII	4	+0·11	2·220	0·10	
23	I	4	+0·03	1·456	0·04	GR
	II	4	−0·09	6·360	0·03	
	III	4	+0·07	3·132	0·05	
	IV	4	+0·06	1·852	0·06	
	V	4	+0·01	0·602	0·03	
	VI	4	−0·01	0·162	0·12	
	VII	4	+0·03	0·528	0·11	
	VIII	4	+0·07	4·929	0·03	
24	I	2	−0·02	0·353	0·06	GR
	II	2	+0·01	0·04	0·04	
	III	2	+0·05	1·179	0·04	
	IV	2	+0·08	0·942	0·08	
	V	2	+0·02	0·202	0·10	
	VI	2	−0·01	1·00	0·01	
	VII	2	+0·13	3·601	0·04	
	VIII	1	0·00			
25	I	4	−0·06	1·899	0·06	GR
	II	4	−0·08	3·265	0·05	
	III	4	+0·04	0·349	0·23	
	IV	4	−0·05	1·091	0·09	
	V	4	+0·05	2·994	0·04	
	VI	4	+0·05	0·855	0·12	
	VII	4	+0·02	0·707	0·06	
	VIII	4	+0·08	2·049	0·07	
26	I	6	−0·14	3·032	0·11	GR
	II	6	−0·10	2·210	0·11	
	III	6	+0·18	2·270	0·19	
	IV	6	+0·02	0·244	0·20	
	V	6	+0·03	0·613	0·12	
	VI	6	+0·10	2·021	0·12	
	VII	6	+0·03	0·296	0·25	
	VIII	6	+0·08	0.077	0·26	
27	I	4	−0·09	4·810	0·04	GR
	II	4	−0·12	2·771	0·09	
	III	4	−0·07	2·555	0·05	
	IV	4	−0·06	2·226	0·05	
	V	4	0·00	0·000	0·04	
	VI	4	−0·06	1·923	0·06	
	VII	4	+0·23	8·534	0·05	
	VIII	4	+0·15	4·471	0·07	
28	I	4	+0·24	2·685	0·18	GR
	II	4	+0·11	1·860	0·12	
	III	4	+0·02	0·185	0·22	
	IV	4	+0·23	5·083	0·09	
	V	4	+0·12	1·563	0·15	
	VI	4	−0·01	0·075	0·27	
	VII	3	+0·06	2·556	0·05	
	VIII	4	−0·01	0·178	0·11	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination of the combustion product*
29	Determinations were done by students and therefore not taken for the calculations					
30	I	4	+0·06	1·073	0·11	GR
	II	4	+0·05	1·091	0·09	
	III	4	+0·05	0·752	0·13	
	IV	4	+0·13	3·043	0·09	
	V	4	+0·11	1·478	0·15	
	VI	4	+0·14	4·179	0·07	
	VII	4	+0·01	0·195	0·10	
	VIII	4	+0·18	5·370	0·07	
31	I	4	−0·09	1·228	0·15	GR
	II	4	−0·12	2·225	0·11	
	III	4	−0·17	2·304	0·15	
	IV	4	+0·22	2·701	0·18	
	V	4	+0·47	2·513	0·37	
	VI	4	+0·18	1·084	0·33	
	VII	4	+0·15	1·946	0·15	
	VIII	4	+0·43	7·544	0·11	
32	I	4	−0·11	1·692	0·13	GR
	II	4	−0·44	2·146	0·41	
	III	4	+0·06	1·200	0·10	
	IV	4	+0·05	2·083	0·05	
	V	4	+0·16	2·406	0·13	
	VI	4	+0·08	1·270	0·13	
	VII	4	+0·08	1·975	0·08	
	VIII	4	+0·12	1·519	0·16	
33	I	4	+0·22	3·492	0·13	GR
	II	4	+0·01	0·187	0·11	
	III	4	+0·07	1·207	0·12	
	IV	5	+0·07	2·029	0·07	
	V	4	+0·12	0·33	0·72	
	VI	4	+0·19	0·540	0·71	
	VII	4	+0·08	1·330	0·12	
	VIII	4	+0·15	2·970	0·10	
34	I	4	+0·09	1·552	0·12	GR
	II	4	+0·11	1·880	0·12	
	III	4	+0·10	1·370	0·15	
	IV	4	+0·11	4·681	0·15	
	V	4	+0·10	2·273	0·09	
	VI	4	+0·15	2·804	0·11	
	VII	4	+0·10	1·709	0·12	
	VIII	4	+0·11	2·651	0·08	
35	I	4	+0·05	1·299	0·08	GR
	II	4	−0·01	0·187	0·11	
	III	4	−0·06	2·609	0·05	
	IV	4	+0·05	0·082	0·12	
	V	4	0·00	0·000	0·05	
	VI	4	+0·17	6·939	0·05	
	VII	4	+0·01	0·046	0·43	
	VIII	4	+0·17	5·000	0·07	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Method of final determination of the combustion product*
36	I	4	−0·22	6·027	0·07	GR
	II	4	−0·21	6·364	0·07	
	III	4	+0·08	2·539	0·06	
	IV	4	−0·12	4·528	0·05	
	V	4	−0·04	1·194	0·07	
	VI	4	−0·15	3·797	0·08	
	VII	4	−0·03	0·833	0·07	
	VIII	4	+0·03	2·222	0·03	
37	I	4	+0·12	2·087	0·12	GR
	II	5	+0·02	0·507	0·09	
	III	4	+0·02	0·851	0·05	
	IV	4	+0·11	3·385	0·07	
	V	4	0·00	0·000	0·07	
	VI	5	+0·08	2·878	0·06	
	VII	4	+0·06	2·308	0·05	
	VIII	6	+0·06	5·469	0·03	
38	I	4	+0·06	1·967	0·06	GR
	II	4	+0·05	2·128	0·05	
	III	4	+0·11	6·660	0·03	
	IV	4	+0·04	0·842	0·09	
	V	4	+0·05	6·470	0·08	
	VI	4	+0·14	4·827	0·06	
	VII	4	+0·09	11·250	0·02	
	VIII	4	+0·07	4·000	0·04	
39	I	4	−0·07	0·560	0·25	GR
	II	4	+0·14	4·912	0·06	
	III	4	+0·08	2·712	0·06	
	V	4	+0·04	0·976	0·08	
40	I	4	+0·16	6·808	0·05	GR
	II	4	−0·88	23·592	0·08	
	III	4	+0·26	2·105	0·25	
	IV	4	+0·02	0·339	0·12	
	V	4	−0·15	1·818	0·17	
	VI	4	+0·09	1·029	0·18	
	VII	4	−0·14	3·420	0·08	
	VIII	4	+0·14	0·259	0·11	
41	I	4	+0·06	2·105	0·06	GR
	II	4	−0·14	1·806	0·16	
	III	4	−0·03	0·612	0·10	
	IV	4	+0·04	0·376	0·21	
	V	4	+0·14	5·185	0·05	
	VI	4	+0·22	11·892	0·04	
	VII	4	−0·02	0·360	0·11	
	VIII	4	+0·21	35·000	0·01	
42	I	4	−0·04	1·212	0·06	GR
	II	4	−0·02	0·381	0·11	
	III	4	+0·02	0·702	0·05	
	IV	4	−0·01	0·333	0·05	
	V	4	+0·03	1·429	0·04	
	VII	4	+0·02	0·727	0·06	
	VIII	4	+0·03	3·000	0·02	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	t	s	*Method of final determination of the combustion product*
43	I	4	+0·28	3·733	0·15	GLC
	II	3	−0·01	0·102	0·17	
	III	3	−0·16	6·159	0·05	
	IV	3	−0·06	6·897	0·01	
	V	3	−0·28	19·404	0·03	
	VI	3	+0·20	6·289	0·03	
	VII	2	+0·06	0·000	0·00	
	VIII	3	+0·22	31·746	0·01	
44	I	4	+0·02	0·038	0·10	GR
	II	4	−0·18	3·871	0·10	
	III	4	+0·02	0·243	0·16	
	IV	4	+0·18	3·130	0·12	
	V	4	+0·13	2·364	0·11	
	VI	4	+0·18	9·729	0·04	
	VII	4	−0·10	3·922	0·051	
	VIII	4	+0·08	2·286	0·07	
45	II	4	+0·01	0·109	0·18	M
	III	4	−0·09	7·377	0·02	
	VII	4	+0·09	3·346	0·05	
46	I	4	−0·02	0·535	0·07	GR
	II	4	−0·10	4·167	0·05	
	III	4	+0·03	0·987	0·06	
	IV	4	+0·07	1·777	0·08	
	V	4	+0·14	7·235	0·04	
	VI	4	+0·15	0·848	0·12	
	VII	4	−0·08	2·744	0·06	
	VIII	4	−0·05	3·533	0·03	
47	I	4	+0·02	0·264	0·15	GR
	III	4	+0·12	2·020	0·11	
	V	4	−0·04	0·632	0·12	
	VII	4	+0·04	1·431	0·06	
48	I	4	−0·08	3·20	0·05	GR
	II	4	−0·06	1·641	0·10	
	III	4	−0·07	2·857	0·05	
	V	4	0·00	0·000	0·05	
	VI	4	−0·04	1·436	0·06	
	VII	4	−0·07	1·724	0·08	
49	I	4	+0·01	0·248	0·08	GR
	II	4	−0·17	1·993	0·17	
	III	4	+0·12	8·163	0·03	
	IV	4	+0·02	1·000	0·04	
	V	4	+0·05	1·005	0·10	
	VI	4	+0·01	0·137	0·15	
	VII	4	+0·11	2·887	0·08	
	VIII	4	+0·04	1·351	0·06	
50	I	4	+0·18	4·215	0·08	GR
	II	5	+0·10	1·573	0·15	
	III	4	+0·41	8·000	0·10	
	IV	4	−0·06	1·149	0·10	
	V	4	+0·10	3·165	0·06	
	VI	4	0·00	0·000	0·13	
	VIII	4	+0·09	3·180	0·06	

Table 4—continued

Laboratory	*Compound*	*Number of determinations*	$\bar{x} - \mu$	*t*	*s*	*Methods of final determination of the combustion product*
51	I	4	−0·05	0·562	0·18	GR
	II	4	−0·08	1·415	0·11	
	III	4	−0·04	0·912	0·09	
	IV	4	+0·06	1·810	0·07	
	V	4	0·000	0·000	0·05	
	VI	4	+0·02	0·166	0·24	
	VII	4	+0·03	0·287	0·21	
	VIII	4	0·00	0·000	0·09	
52	I	3	0·00	0·000	0·08	GR
	II	3	−0·36	12·457	0·05	
	III	2	+0·01	0·353	0·03	
	IV	2	+0·05	3·546	0·01	
	V	3	+0·19	9·510	0·03	
	VI	2	+0·05	0·393	0·13	
	VII	3	−0·02	0·693	0·05	
	VIII	2	−0·18	1·950	0·09	
53	I	4	+0·08	1·347	0·12	GR
	II	4	−0·04	0·895	0·09	
	III	3	−0·05	2·747	0·03	
	IV	3	−0·03	3·297	0·02	
	V	4	+0·10	4·255	0·05	
	VI	2	+0·12	3·324	0·04	
	VII	4	+0·13	1·704	0·15	
	VIII	3	+0·03	0·544	0·10	
54	I	4	+0·13	1·879	0·14	GR
	II	4	−0·10	0·684	0·29	
	III	4	−0·28	2·914	0·16	
	IV	4	+0·23	4·236	0·11	
	V	4	+0·04	0·537	0·15	
	VI	4	−0·02	0·421	0·09	
	VII	4	+0·19	15·510	0·02	
	VIII	4	+0·12	1·103	0·22	
55	I	4	+0·02	1·786	0·02	GR
	II	4	+0·04	1·600	0·05	
	III	4	+0·03	3·000	0·02	
	V	4	+0·00	0·000	0·01	
	VIII	4	+0·06	4·526	0·03	
56	I	4	−0·08	0·423	0·38	GR
	II	4	+0·03	0·427	0·14	
	III	4	−0·01	0·205	0·10	
	IV	3	+0·30	3·400	0·15	
	V	4	+0·01	0·195	0·10	
	VI	4	+0·11	1·350	0·16	
	VII	4	+0·20	1·641	0·24	
	VIII	4	+0·12	10·710	0·02	
57	I	4	−0·01	0·384	0·15	GR
	II	4	−0·15	13·391	0·02	
	III	4	−0·02	1·426	0·04	
	IV	4	+0·04	2·213	0·04	
	V	4	−0·04	1·597	0·05	
	VI	4	+0·05	2·083	0·05	
	VII	4	−0·05	2·771	0·04	
	VIII	4	+0·07	1·761	0·08	

0·05:

for 4 determinations	3·182
for 5 determinations	2·776
for 6 determinations	2·571
for 7 determinations	2·447

GR	gravimetric methods
COND	conductometric methods
GLC	methods with gas chromatography finish
M	manometric methods
TITR	titrimetric methods

The distribution of the deviations of the means is shown in *Figures 1* and *2* for gravimetric techniques and for other techniques (e.g. electrical conductivity, thermal conductivity after gas-chromatography separation, manometry and titrimetry). For the gravimetric technique, the results for the estimation of significant deviations are collected in *Table 5*. Systematic errors in the determination of carbon in compounds III, IV, V, VII and VIII, and in the determination of hydrogen in compounds II, III, V, VI and VIII, were found in over 25 per cent of the laboratories involved. This statistical treatment was only done when the number of gravimetric determinations made was sufficient.

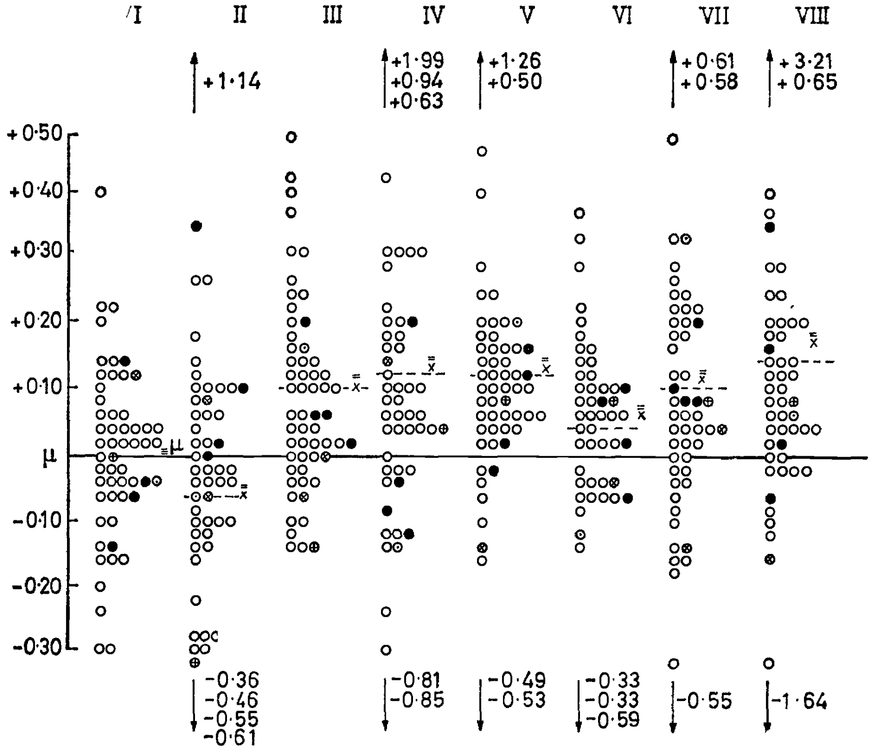

Figure 1. Carbon determination in substances I–VIII. The distribution of the frequencies of differences $\bar{x} - \mu$. The final determination of the combustion products [gravimetric ○; conductometric ●; heat conductivity ⊙; manometric ⊗; titrimetric ⊕]

2.2 Deviation of final means; standard deviations

The systematic errors found in a relatively high proportion of the laboratories involved, made it necessary to estimate the significance of the deviations of the means for all laboratories. *Tables 6* and *7* show the deviations of the means for compounds I–VIII and the corresponding values of *t* used to estimate the significance of these deviations. All the deviations given have a

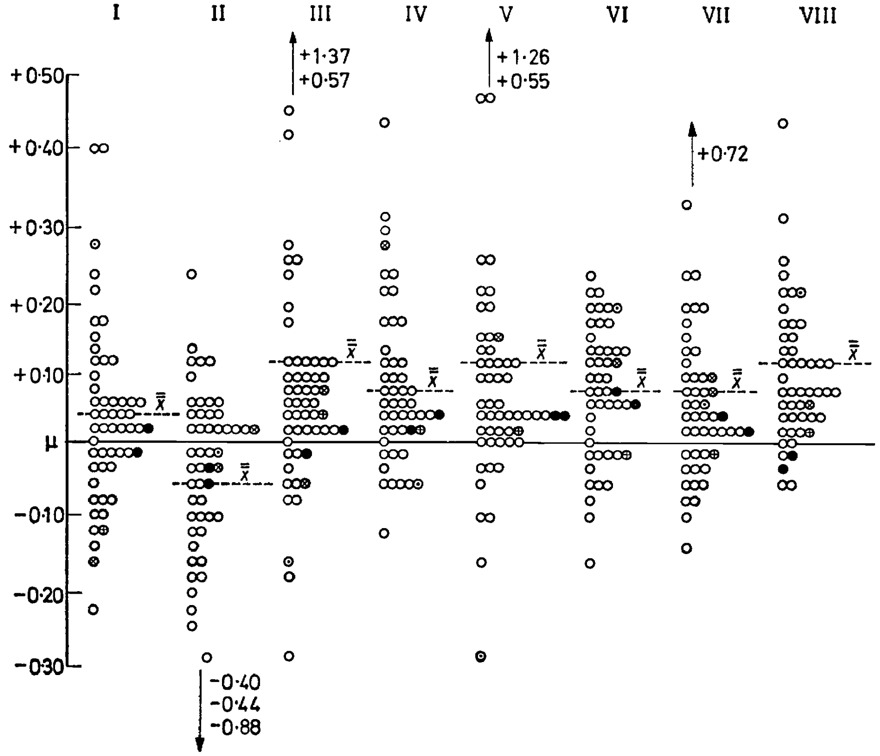

Figure 2. Hydrogen determination in substances I–VIII. The distribution of the frequencies $\bar{x} - \mu$. The final determination of the combustion products [gravimetric ○; conductometric ●; heat conductivity ⊙; manometric ⊗; titrimetric ⊕]

Table 5. Frequency of systematic error

Compound	*Number of laboratories*	*Number of laboratories with systematic error*	%
	DETERMINATION OF CARBON		
I	48	4	8·3
II	46	10	21·7
III	49	16	32·7
IV	44	16	36·4
V	49	14	28·6
VI	42	8	19·0
VII	44	13	29·5
VIII	43	16	37·2
	DETERMINATION OF HYDROGEN		
I	48	10	20·8
II	46	12	26·0
III	49	13	26·5
IV	44	11	25·0
V	49	15	30·6
VI	42	13	31·0
VII	44	11	25·0
VIII	43	17	36·1

confidence level of 0·05 (95 per cent) except for the determination of carbon in anthracene. This will be discussed further on p. 71. *Tables 6* and *7* also show the standard deviations calculated from the results for carbon and hydrogen in all compounds.

Table 6. Determination of carbon—survey of the results found for particular compounds by the gravimetric method

Compound	*Number of laboratories*	*Number of determinations*	$\bar{x} - \mu$	t	s^2	s	F
I	48	196	+0·003	—	0·0519	0·23	—
II	46	193	−0·048	2·184	0·1075	0·33	2·071
III	49	200	+0·093	6·445	0·0383	0·19	1·355
IV	44	175	+0·116	6·287	0·1978	0·44	3·811
V	49	198	+0·118	7·812	0·0798	0·28	1·538
VI	42	166	+0·036	2·153	0·0514	0·23	1·009
VII	44	184	+0·079	4·606	0·0677	0·26	1·304
VIII	43	178	+0·137	2·630	0·4463	0·67	8·999

t_{120} = 1·980, $F_{120}{}^{120}$ = 1·352 (0·05)

Table 7. Determination of hydrogen—survey of results found for particular compounds by the gravimetric method

Compound	*Number of laboratories*	*Number of determinations*	$\bar{x} - \mu$	t	s^2	s	F
I	48	196	+0·038	3·363	0·0316	0·18	—
II	46	193	−0·056	5·018	0·0461	0·21	1·459
III	49	200	+0·109	6·050	0·0667	0·26	2·110
IV	44	175	+0·083	8·200	0·0220	0·15	1·436
V	49	198	+0·119	7·069	0·0607	0·25	1·921
VI	42	166	+0·074	6·912	0·0230	0·15	1·374
VII	44	184	+0·066	6·230	0·0351	0·19	1·111
VIII	43	178	+0·106	10·515	0·0195	0·14	1·621

t_{120} = 1·980, $F_{120}{}^{120}$ = 1·352 (0·05)

The corresponding scatter of the results (expressed as the square of the standard deviation) was compared with the scatter obtained for anthracene. In the case of carbon, the scatters found were (except for compounds VI and VII) considerably greater than those found for anthracene. In the determination of hydrogen, the scatters of the results for compounds II, III and V were significantly higher than those for anthracene, whereas the scatters for compounds IV, VI and VIII were narrower. These results are discussed in more detail on p. 71.

3. DISCUSSION OF METHODS, INDIVIDUAL ANALYTICAL OPERATIONS AND THE RESULTS OF DETERMINATIONS ON STANDARD SUBSTANCES

3.1 Methods of combustion

All the methods used involved combustion with a catalytic substance. The fillings of the combustion tubes are listed in *Table 8*. Most collaborators (27) used the classical copper oxide filling; others used the Co_3O_4 filling (12 collaborators) and the silver permanganate decomposition product filling (6 collaborators).

Table 8. Determination of carbon and hydrogen using tubes with catalytic fillings

Results no.	*Catalyst*	*Temperature* (°C)	*Length of filling* (cm)	*Gas flow* (ml/min)	*Amount of gas for one determination* (ml)
1	CuO	700	18	5	200
3	CuO	775	—	7	150–250
4	CuO	800	13·5	10	225
6	CuO	850	12	7	175
7	CuO	670–850	11·5	5–7	250
8	Co_3O_4,$AgMnO_4$	750	10·5;7·5	12	150
9	$AgMnO_4$	500–600	5	12	300
10	Co_3O_4	600	5	15	200
11	Pt	750	27	6	200
12	Pt	850	14	50–100	500
13	Co_3O_4,Pt	760	3;13	5	170
14	CuO	700	22	50	750
15	Co_3O_4	800	9	10	150
17	CuO	920	13	10–12	150–180
18	CuO	550	20	140	
19	$AgMnO_4$	525	3·5	30	
21	NiO	700–750	14	20–30	300–400
22	Co_3O_4	750	5	80	100
27	CuO + WO_3	820	19	2·5	200
28	CuO, $AgVO_3$	850–900	—	15	313
29	Co_2O_3	700	8	10–12	150
30	CuO	660	15	4	150
32	CuO	800	30	10	300
34	Co_3O_4	700		8–10	220–230
35	CuO	840–880	35	—	294
36	Co_3O_4	800	18	12	180
38	CuO	850	25	150	700
39	Co_3O_4	700	4	10–14	180
42	CuO, Pb_3O_4	850	19	8	400
43	$AgMnO_4$	550	6	15–20	200–250
44	$AgMnO_4$	750	15	4	290
45	CuO, $AgVO_3$	830–895	12	10–100	450
48	CuO	680	14	10	210
50	CuO	650	15	10	400
51	CuO	880	19	15	450
52	Co_3O_4	850	10	50	500
53	Co_3O_4	700	—	—	300
54	Co_3O_4, $AgMnO_4$	800–500	20–22·5	12	180
55	CuO	650	15	4	120
56	CuO	850	12·5	6	270
57	CuO, CeO_2	800	18	8	200

The analytical results for the standard samples indicate that all the catalysts used ensure quantitative combustion of compounds I and III–VIII. The decisive factors in the successful use of a particular catalyst are (a) an appropriate length of layer, (b) the quality of the active surface of the material used, (c) the gas flow rate. The working conditions used in the different laboratories (see *Table 1*) varied widely.

The average results of all the determinations of cholesterol were found to be lower than the true value; only for this compound were low results found to an extent which is statistically significant. The low results for carbon in this compound may be due to various factors: (a) too low a temperature of combustion; (b) an insufficient volume of carrier gas (cholesterol has a slow combustion rate so that flushing the combustion products into the absorption vessels may take longer than usual); (c) choice of catalyst; (d) impurity of the sample (this possibility was not considered).

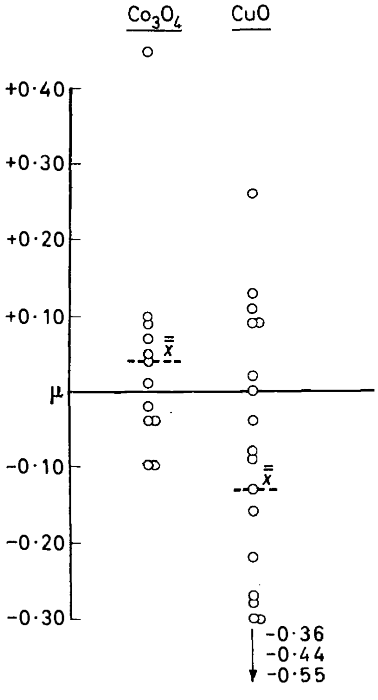

Figure 3. Carbon determination in cholesterol. The effect of the catalytic filling of the tube

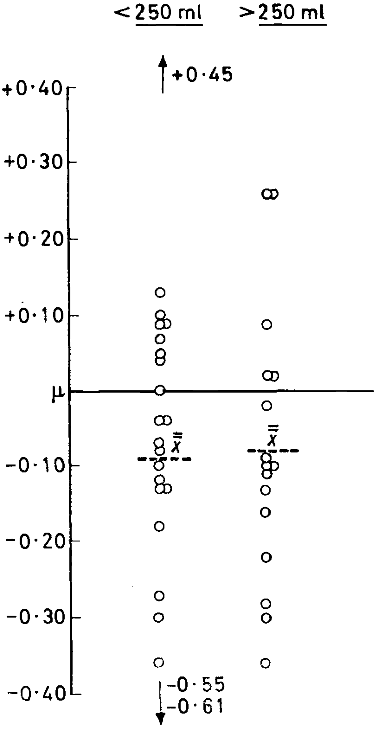

Figure 4. Carbon determination in cholesterol. The effect of amount of gas used

In a further study of the negative deviations of the average results from the theoretical values, the procedures involving a gravimetric determination were chosen. The data are shown in *Table 9*. *Figures 3, 4* and *5* show the mean results obtained in different laboratories in relation to factors (a), (b)

Table 9. Determination of carbon in cholesterol

	Number of laboratories	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_D	t_{Dtab}
EFFECT OF CATALYTIC FILLING										
CuO	20	84	−0.126	4·007	2·000	0·0896	1·514	1·637	3·532	1·980
Co_3O_4	12	48	+0·043	1·372	2·021	0·0592				
INFLUENCE OF AMOUNT OF GAS USED										
<250 ml	23	97	−0·085	2·882	1·980	0·0942	1·463	1·467	0·208	1·980
>250 ml	16	64	−0·076	2·630	2·000	0·0644				
EFFECT OF TEMPERATURE OF COMBUSTION										
<750°C	18	75	−0·091			0.1021	1·545	1·352	0·527	1·980
>750°C	21	86	−0·068	2·611	1·980	0·0661				

and (c) listed above. It is obvious that the deviations of the means from the true value are significant when copper oxide or cobalt oxide was used as catalyst. The influence of temperature or the total volume of sweeping gas was not a governing factor; this conclusion was reached from the qualitative trends in the results and was confirmed statistically. The precision of the results was poorer when the temperature of the catalyst was less than 750°C; it therefore appears that the low results for carbon are caused by the catalyst being insufficiently active to ensure quantitative combustion. Difficultly combustible materials (e.g. cholesterol derivatives) are thought to split off methane (from angular methyl groups) on heating. It has been shown that methane is the most difficult to decompose of all organic materials and this may be the cause of the low results.

3.2 The removal of nitrogen oxides

The various procedures used in the collaborating laboratories for the removal of nitrogen oxides are shown in *Table 10*. Absorption on manganese dioxide was used by half the laboratories (25 per cent), 18 used lead dioxide and others used less common methods. As was mentioned in Section 2·2 (see also *Table 7*) the range of individual results for hydrogen in 2,4-dinitrophenylhydrazine was wider ($s = \pm 0{\cdot}26$) than for other standards.

Table 10. Reagents for removal of nitrogen oxides

Reagent	*Laboratory*
PbO_2	1, 11, 15, 16, 18, 28, 30, 31, 32, 33, 37, 41, 48, 52, 54, 55, 56, 57
$PbCrO_4 + CuO$	29
MnO_2	2, 3, 4, 6, 7, 9, 10, 12, 13, 17, 19, 22, 24, 25, 26, 27, 34, 36, 38, 40, 42, 46, 49, 50
Cu	20, 23, 45
Diphenylamine —H_2SO_4	8
H_2SO_4 conc.	21
Hydroxylamine sulphate on silica gel	14

The deviation of the average result is also higher than usual (+0·109). Both these figures are statistically significant†.

It is known that high results for hydrogen are usually obtained for nitrogen-containing compounds when manganese dioxide is used to remove nitrogen oxides (partial absorption of nitrogen oxides). Accordingly, the methods using manganese dioxide and lead dioxide were compared for the case of 2,4-dinitrophenylhydrazine (see *Table 11* and *Figure 6*).

When lead dioxide was used, the deviation of the mean for hydrogen was +0·072, compared with +0·111 for manganese dioxide; both deviations are statistically significant but the mutual difference may not be significant.

---

† From the data submitted by the collaborating laboratories it was not possible to determine whether a correction was applied for the amount of nitrogen oxide absorbed on the magnesium perchlorate.

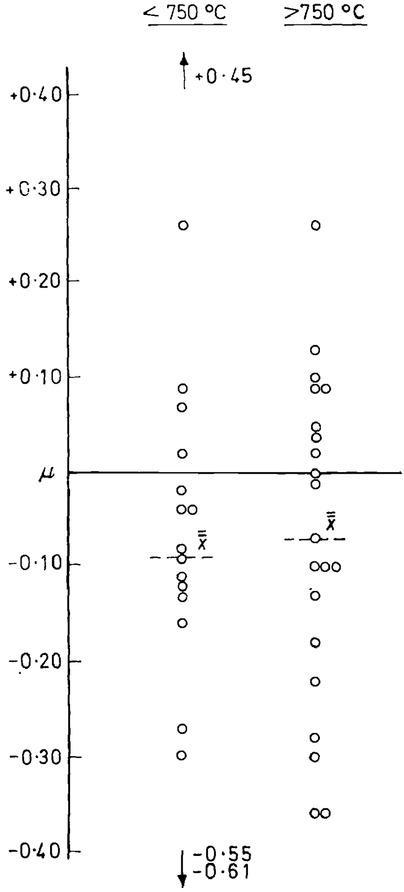

Figure 5. Carbon determination in cholesterol. The effect of combustion temperature

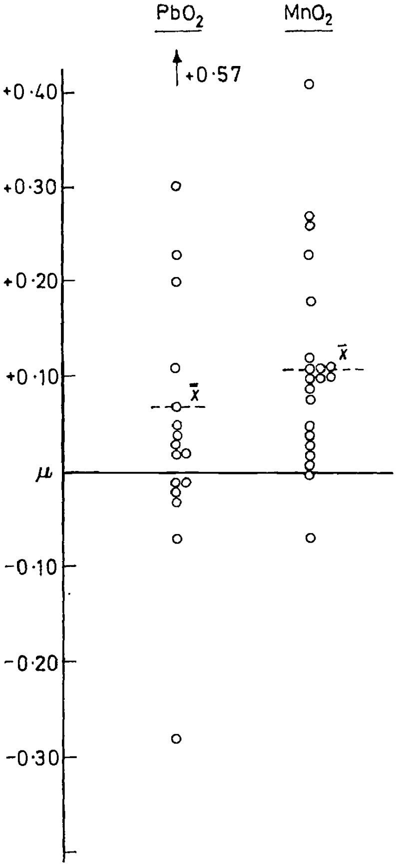

Figure 6. Hydrogen determination in 2,4-dinitrophenylhydrazine. The use of PbO_2 or MnO_2 for trapping nitrogen oxides

The results with manganese dioxide are more precise than those with lead dioxide (the ratio of the variances is significant). Both methods gave high results for carbon (the deviation of the mean is significant); in contrast to the case with hydrogen, the mutual difference is here statistically significant (*Table 11*, *Figure 7*). For carbon, the two methods are of virtually the same precision (ratio of variances is not significant). The conclusion can be made that manganese dioxide should be preferred to lead dioxide in the analysis of nitrogen-containing compounds: the results are more precise for hydrogen and more accurate for carbon.

3.3 Separation of halogens and sulphur oxides

The methods used for the separation of halogens are summarized in *Table 12.* It is known that iodine is difficult to absorb on silver and that silver iodide tends to dissociate at the working temperature (500–600°C), hence

Table 11. Determination of hydrogen and carbon in 2,4-dinitrophenylhydrazine. The use of PbO_2 or MnO_2 for absorption of nitrogen oxides

	Number of laboratories	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_D	t_{Dtab}
			DETERMINATION OF HYDROGEN							
PbO_2	17	66	+0·072	2·993	2·000	0·0462	1·949	1·534	1·437	1·980
MnO_2	22	91	+0·111	7·322	1·980	0·0237				
			DETERMINATION OF CARBON							
PbO_2	17	66	+0·112			0·0312	1·285	1·467	2·036	1·980
MnO_2	22	91	+0·053	2·629	1·980	0·0401				

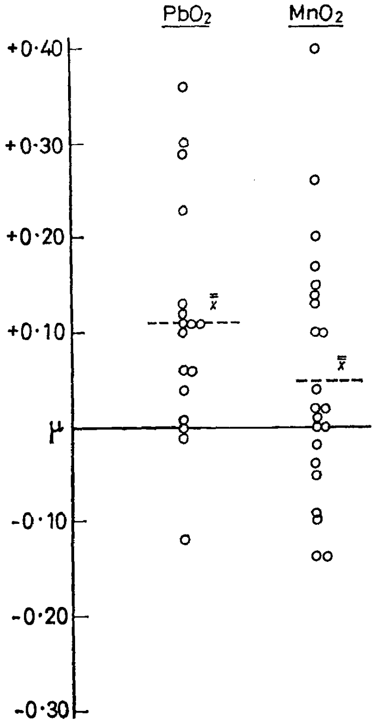

Figure 7. Carbon determination in 2,4-dinitrophenylhydrazine. The use of PbO_2 or MnO_2 for trapping nitrogen oxides

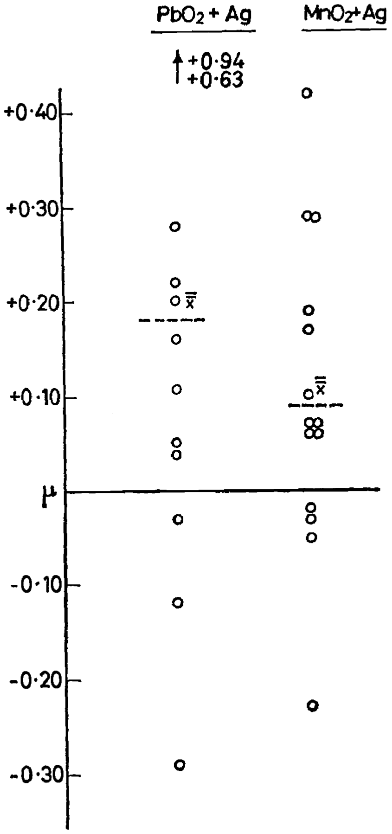

Figure 8. Carbon determination in *o*-iodobenzoic acid. The effect of the use of (PbO_2 + Ag) and (MnO_2 + Ag) respectively

o-iodobenzoic acid was included in the study. The deviation of the mean carbon result was +0·116, which is, of course, statistically significant; obviously, iodine is not completely absorbed and passes to the carbon dioxide absorber. In order to discover whether or not the high carbon results were influenced by the use of lead dioxide or manganese dioxide in

Table 12. Reagents for removal of halogens and sulfur oxides

Laboratory No.	*Reagent*	*Temperature (°C)*	*Laboratory No.*	*Reagent*	*Temperature (°C)*
1	Electrolytic Ag	700	14	Ag woo	600
17		530	15		500
39		500	19		525
40		750	22		750–500
2	Ag	650	30		660
4		800	37		650–700
7		600	50		650
10		600	55		130–550
20		600	51	Ag on pumice	490
27		570	5	Ag net	300
29		520	21		400–500
32		450	18	Ag_2O	150
34		700	36	$AgMnO_4$	550
38		600–300	43	$AgMnO_4$ + Ag	550–500
42		850	44	$AgMnO_4$ + Ag	550
46		700	54	$AgMnO_4$ + Ag	500
48		680	45	$AgMnO_4$, $AgVO_3$, Ag	830
52		550	28	$AgVO_3$ + Ag	*c.* 700
53			12	$AgVO_3$ + Ag	850
56		850	35	$AgVO_3$ + Ag	840, 840–150
6		300–400	25	$PbCrO_4$	350
8		700	3	$PbCrO_4$, Ag, Pb_3O_4	775
9		500	49	CeO_2, perhydrite	300
13		500			

the method, the results obtained when silver was used for iodine absorption and one of the dioxides was used for absorption of nitrogen oxides, were treated statistically (*Table 13, Figure 8*). It is obvious that the values of the means (+0·183 for lead dioxide and +0·093 for manganese dioxide) differ significantly. This means that traces of iodine escaping from silver are absorbed in manganese dioxide fillings. However, there is no difference in the precisions of the determinations in the two cases ($S_{PbO_2} = \pm 0{\cdot}36$; $s_{MnO_2} = \pm 0{\cdot}24$).

Table 13. Determination of carbon in iodobenzoic acid and in sulphanilamide. Effect of the use of PbO_2 + Ag or MnO_2 + Ag

	Number of laboratories	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_D	$t_{D tab}$
			DETERMINATION OF CARBON IN IODOBENZOIC ACID							
PbO_2 + Ag	12	46	+0·183	3·916	2·021	0·1306	2·180	1·594	1·647	1·980
MnO_2 + Ag	14	55	+0·093	2·995	2·000	0·0599				
			DETERMINATION OF CARBON IN SULPHANILAMIDE							
PbO_2 + Ag	11	46	+0·235	—	—	0·0599	2·155	1·594	3·122	1·980
MnO_2 + Ag	15	57	+0·114	4·959	2·000	0·0278				

For the determination of carbon in sulphanilamide, methods in which a combination of lead dioxide and silver was used, gave results significantly different from the true value. A combination of silver and manganese dioxide gave results which were more accurate and more precise (*Table 13, Figure 9*).

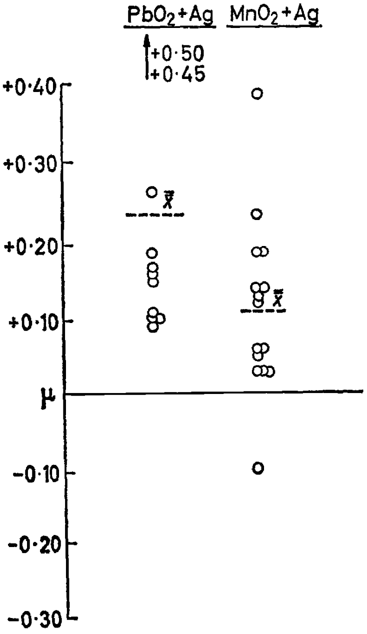

Figure 9. Carbon determination in sulphanilamide. The effect of the use of ($PbO_2 + Ag$) and ($MnO_2 + Ag$) respectively

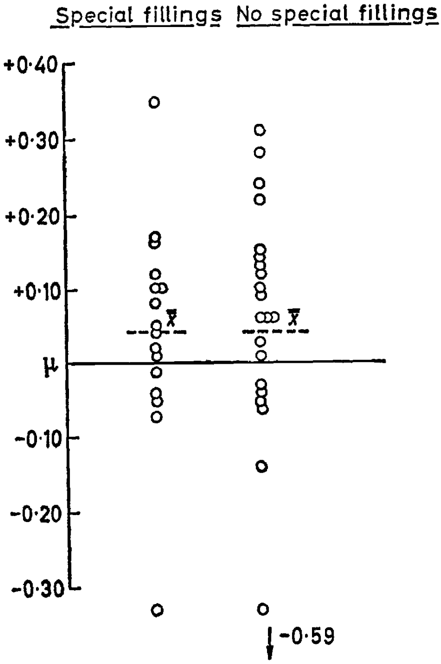

Figure 10. Carbon determination in *p*-fluorobenzoic acid. The effect of the use of special fillings

For *p*-fluorobenzoic acid, the deviation of the mean result for carbon (+0·036) is not significant. The results obtained with special fillings (*Table 14*, *Figure 10*) were slightly more precise.

3.4 Analysis of compounds containing phosphorus and potassium

The mean result for carbon in triphenylphosphate is +0·079 per cent higher than the true value. This statistically significant result may be due to the passage of acidic vapours into the carbon dioxide absorber (as in the case of nitrogen, sulphur and halogen compounds). This suggestion needs further evidence for substantiation. (In a sample of 5 mg of triphenylphosphate, the +0·081 per cent error observed corresponds to $4 \mu g$ P_2O_5). The results were found to be significantly higher (+0·164 per cent) when vanadium pentoxide or tungstic oxide was added to the sample in the boat (see *Table 14*, *Figure 11*).

For the determination of hydrogen, the precision ($s = \pm 0{\cdot}19$) and accuracy (+0·666) are within the normal range for the other standards.

In 17 cases (35 per cent), the sample was analysed without any addition to the sample boat; tungstic oxide was added in 21 cases (44 per cent); vanadium pentoxide was added in 5 cases and other additives were used in

Table 14. Determination of carbon in *p*-fluorobenzoic acid, in triphenylphosphate, and in potassium hydrogen phthalate. Effect of the combustion additives

	Number of laboratories	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_D	$t_{D\text{tab}}$
		DETERMINATION OF CARBON IN *p*-FLUOROBENZOIC ACID								
Additives	16	66	+0·044	1·989	2·000	0·0411	1·547	1·467		
No additives	22	90	+0·035	1·341	2·000	0·0636				
		DETERMINATION OF CARBON IN TRIPHENYLPHOSPHATE								
V_2O_5, WO_3	19	76	+0·164	5·674	2·000	0·0682	1·001	1·534	5·182	1·980
No additives	19	81	0·000			0·0681				
		DETERMINATION OF CARBON IN POTASSIUM HYDROGEN PHTHALATE								
V_2O_5	9	36	+0·109	3·993	2·042	0·0309	1·285	1.740	0·951	1·980
WO_3	20	84	+0·077	4·132	2·000	0·0397				

5 cases. It is clear that the addition of auxiliary oxidants is not necessary for samples of the triphenylphosphate type. Impurities coming from the auxiliary oxidant caused high results. However, this finding does not hold in general for phosphorus-containing compounds.

When potassium hydrogen phthalate was analysed, the normal precision was obtained for hydrogen, but the precision of the carbon results was much less (for C, $s = \pm 0{\cdot}67$; for H, $s = \pm 0{\cdot}14$). The poor precision for carbon was caused by the use of acid additives for the liberation of carbon dioxide from the metal carbonate. The additives also caused an increase (+0·106) in the results for hydrogen (presumably because of inadequate drying of the reagent). The mean carbon result was +0·137 per cent higher than the true value, probably because of traces of organic impurities in the compounds added to the sample (WO_3, V_2O_5). The average result for carbon in 36 determinations with vanadium pentoxide was found to be +0·109 per cent above the true value, whereas the average result of 84 determinations in 20 laboratories with tungstic oxide was found to be +0·077 per cent high; the difference between these mean results is not significant (see *Table 14* and *Figure 12*). It is therefore not possible to explain

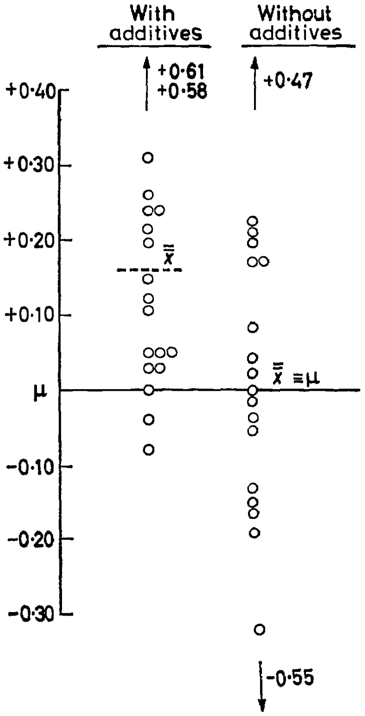

Figure 11. Carbon determination in triphenylphosphate. The effect of the use of additives in the combustion boat

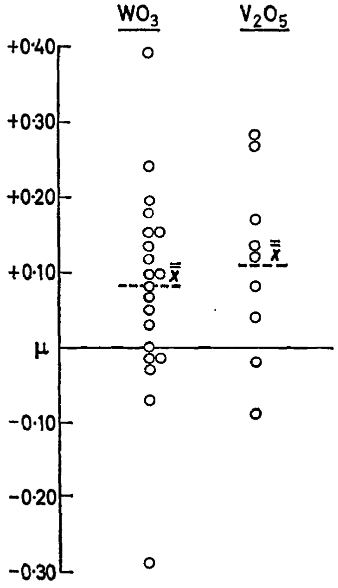

Figure 12. Carbon determination in potassium hydrogen phthalate. The effect of the use of additives in the combustion boat

the statistically significant high result for carbon in potassium hydrogen phthalate. Further experimental work is needed to decide if the high carbon results obtained for compounds containing halogens, sulphur, nitrogen and phosphorus are caused by the presence of these elements.

Almost half the collaborating laboratories (46 per cent) used tungstic oxide as additive; vanadium pentoxide was used by 20 per cent of the laboratories while others used different additives. In 7 cases, the analyses were done without any additives. Clearly, tungstic oxide is the most commonly used reagent for the liberation of carbon dioxide from components containing alkali metals.

3.5 Treatment of weighing vessels in gravimetric determination

Twenty-five laboratories gave information on the method of weighing the absorption tubes for the determination of carbon. In 9 cases, the absorption tube was wiped; it was not wiped in 16 cases. The precision and accuracy were the same in both groups as shown for analyses of anthracene (*Table 16*, *Figure 14*).

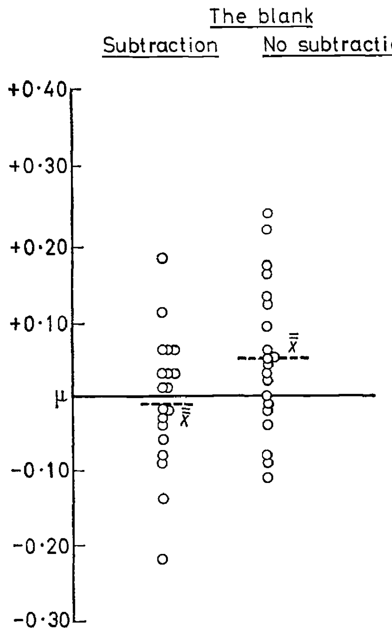

Figure 13. Hydrogen determination in anthracene. The effect of substraction of the blank

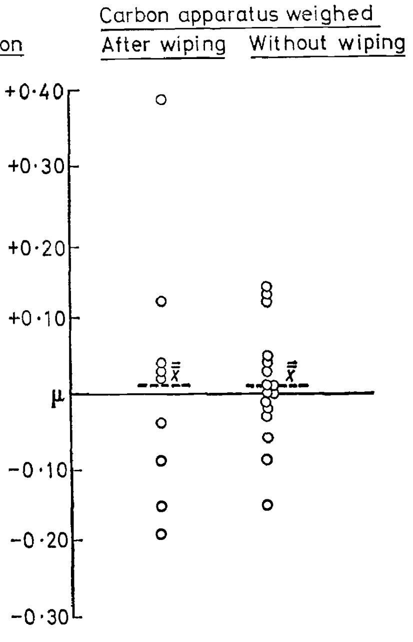

Figure 14. Carbon determination in anthracene. The effect of wiping the absorption tube

3.6 Survey of other methods of final determination

Although gravimetric methods predominated, several other methods of completing the determinations were used. Two collaborators used a manometric method on the ultramicro scale. One collaborator used a titrimetric process. In one case the carbon and hydrogen were determined by thermal conductivity after a gas-chromatographic separation, and in three

Table 15. Determination of hydrogen in anthracene. Effect of correction for blank experiment

Blank	*Number of laboratories*	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_{D}	$t_{\mathrm{D\,tab}}$
Subtracted	19	81	−0·006			0·0161	1·652	1·534	2·755	1·980
Not subtracted	20	81	+0·052	3·172	2·000	0·0261				

Table 16. Determination of carbon in anthracene. Effect of wiping the carbon dioxide absorption vessels

Weighing of absorption vessels	*Number of laboratories*	*Number of determinations*	$\bar{x} - \mu$	t	t_{tab}	s^2	F	F_{tab}	t_{D}	$t_{\mathrm{D\,tab}}$
After wiping	9	36	+0·014	0·400	2·021	0·0512	1·280	1·594	0·074	1·980
Without wiping	16	70	+0·011			0·0400				

cases, changes in electrical conductivity after absorption of carbon dioxide and water were measured.

The standard deviations of the carbon results were lower by the electrical conductivity methods than by the gravimetric method, while the standard deviations obtained by the manometric, titrimetric and chromatographic methods were close to that of the gravimetric method (see *Figure 1*).

4. CONCLUSIONS

Precise results for the determination of carbon and hydrogen are obtained in most laboratories, indicating that adequate methods are in common use. Where precision is less satisfactory, the cause must be sought in some peculiar working condition in a particular laboratory, because this study has shown that the precision of one particular method may vary from place to place.

The study has indicated that there is no doubt about the theoretical bases of the methods used. It does appear, however, that it is impossible to use manganese dioxide to remove nitrogen oxides when water is absorbed on to phosphorus pentoxide. The data collected on the various methods allow an assessment of the general suitability of individual conditions (e.g. types of balance, weighing temperature, combustion conditions, catalysts, etc.).

The large quantity of data allows conclusions to be drawn, which may be important for the further development of elemental analysis. For example, it has been shown that the accuracy and precision of the determinations depends to some extent on the elemental composition of the compound being analysed. It has been definitely established that the overall mean of the carbon values is higher than the true value in compounds containing S, I, N, P and K, whereas the average carbon result for cholesterol is lower than the true value. The determinations of hydrogen show a positive deviation (which is probably proportional to the hydrogen content of the samples used) and this error is undoubtedly higher in nitrogen-containing compounds. Methods in which lead dioxide is used for absorption of nitrogen oxides show a wider range of results for the determination of hydrogen than methods in which manganese dioxide is used.

The high results obtained in the analysis of compounds containing S, I, N and P call for further investigation. The low results obtained for compounds of the cholesterol type should also be studied, though this error is probably caused by inefficient combustion catalysts. The small deviations and errors disclosed by the present statistical treatment could be studied by means of sensitive analytical techniques such as infrared spectroscopy, gas chromatography, etc. Experiments with appropriate standard compounds would allow definite conclusions to be drawn about the concentration dependence of errors. These would seem to be more profitable areas for further research than the development of further modifications of present methods.

The present study has also indicated that the simple deduction of a blank value is not valid. Proper corrections can be made only on the basis of regression analysis of results, unless the general validity of a calculated correction can be proved by long-term experiment.

However, the use of corrections should be regarded as only a temporary expedient. It would be much more suitable to introduce new methods in order to decrease systematic errors and errors caused by elemental composition. As far as this study is concerned the majority of the participating laboratories still used the classical techniques. Less than one half employed rapid combustion on more effective catalysts in a fast oxygen stream. Further, the possibility of more efficient reagents for the absorption of halogens, sulphur oxides and nitrogen oxides should be studied and the optimal conditions for quantitative chemical reaction established. Methods of decreasing the pressure of water vapour over the drying agent (anhydrone) are needed as well as stabilized conditions of weighing absorption apparatus. Alternatively, precise non-gravimetric procedures could be used.

Further investigations of precision and accuracy of the new automatic methods which have recently been introduced and of methods for the determination of other elements would be very useful.