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Study of Carbon, Hydrogen and Nitrogen Determination by Combustion-Gas Chromatography*

By

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With 6 Figures

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In the early sixties numerous articles were written^{1,2} on the application of gas chromatography to elemental microanalysis. However, after further knowledge was gained, a highly critical attitude began to arise towards the methods of combustion combined with gas chromatography. The reasons may be stated as follows:

(1) instantaneous combustion was judged impossible because of the presence of a carrier gas such as helium; it was therefore impossible to start the chromatography with a homogeneous mixture of the combustion gases;

(2) insufficient oxidative power of the system; substances difficult to burn and samples over 1 mg were incompletely combusted;

(3) difficulties in separating the individual gases N_2 , CO_2 and H_2O in a single step;

(4) adsorption phenomena which interfered with the gas chromatographic separation;

(5) high blank values traced back to the use of oxidizing additives;

(6) disturbances of the pressure-equilibrium of the system due to the intermittent introduction of the samples;

(7) the manual evaluation of the chromatogram was inaccurate and time-consuming;

* Dedicated to the memory of Dr. Wolfgang Schöniger.

(8) combustion under dynamic conditions was judged inappropriate for measuring the response signal;

(9) the measurements were relative, and the area integrals had to be compared with those of standard compounds.

This criticism brought forth many studies on improvements and modifications to the method. Improvements included: direct measurement of the H_2O by thermal conductivity, avoiding conversions³; increase in the oxidative capacity of the system⁴; the use of new stationary phases⁵; the electronic integration of the signal, with digital print-out⁶; the use of automatic samplers⁷; the elimination of oxidizing reagents⁸, and the frontal technique of measuring effluent gases⁹.

Modifications included: a trap for the combustion gases was placed in front of the gas chromatographic section to produce a homogeneous gas mixture; gas chromatographic separation was replaced with other separation methods; the dynamic mode was replaced by the static mode, both for combustion and for gas measurement. At the present time, it may safely be said that some of the critical points, namely (3), (5), (6), (7) have been virtually resolved.

We use a commercially available automatic analyser, which already contains improvements in respect of points (3), (6), (7), and have attempted to improve the method, bearing in mind critical points (1), (2), (4), (5), (8). This study provided useful guidelines for adopting a faster and safer combustion, increasing the oxidative capacity of the system, and selecting oxidizing and reducing reagents suitable for use in the combustion — gas chromatographic method.

Principle of the Method

The organic samples are packed into lightweight containers of oxidizable metal, and dropped at preset times into a vertical quartz tube, heated to $1050^{\circ}C$, through which a constant flow of helium is maintained. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen. Flash combustion takes place, primed by the oxidation of the container. Quantitative combustion is then achieved by passing the gases over Cr_2O_3 .

The mixture of the combustion gases is transferred over copper at $640^{\circ}C$ to eliminate excess of oxygen then, without stopping, it is introduced into the chromatographic column, heated to about $120^{\circ}C$ and filled with a vinyl ethyl benzene-divinyl benzene polymer as stationary phase. The individual components are then separated,

eluted in the order $N_2-CO_2-H_2O$, and measured by a thermal conductivity detector. The response signal feeds a potentiometric recorder and in parallel an integrator with digital print-out. The instrument is calibrated by combustion of standard compounds.

Apparatus

An Elemental Analyser, model 1102 (C. Erba, Milan, Italy) was used; its scheme is given in Fig. 1. This instrument automatically determines carbon, hydrogen and nitrogen. Combustion of the sample, separation of the com-

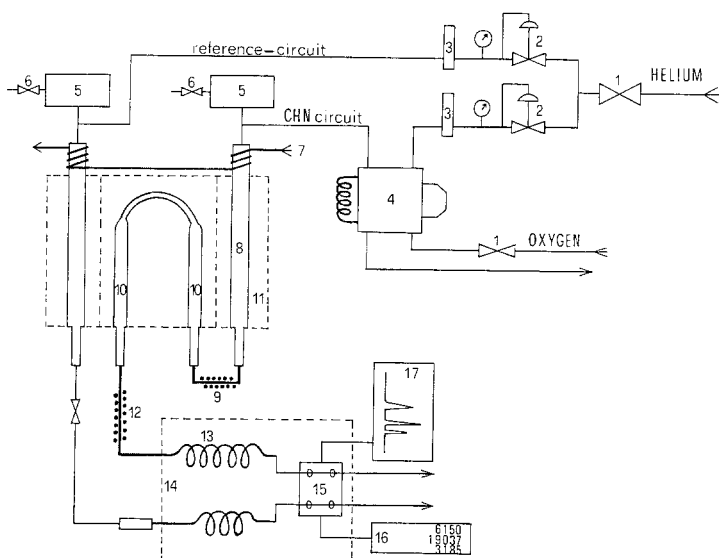


Fig. 1. Scheme of the apparatus

(1) Pressure regulator; (2) Flow controller; (3) Purification tubes; (4) Oxygen injection valve; (5) Sample dispenser; (6) Sweeping valve; (7) Water cooler; (8) Oxidation reactor; (9) Heated connecting tubing; (10) Reduction reactor; (11) Oven for oxidation reactor; (12) Heated tubing; (13) CHN chromatographic column; (14) Thermostatically controlled oven; (15) Thermal conductivity detector; (16) Digital integrator-printer; (17) Recorder

bustion gases and measurement by thermal conductivity are all carried out in the dynamic mode. The reference side is used in the instrument as part of another permanent analytical circuit for oxygen determination. There are thus two analytical circuits, one for CHN determination, and the other for oxygen. They do not work simultaneously, but alternately as analytical and reference circuits. The oxygen circuit, described elsewhere¹⁹, is considered in this work only as a reference circuit.

The CHN circuit consists of two gas sources, for helium and oxygen, an oxygen dispenser valve for periodic injection, an automatic sampler, an in-

dependently heated vertical oxidation reactor, a vertical U-shaped reduction reactor, a gas chromatographic column and a detector, both housed in a thermostatically controlled oven, and a recording-measuring system.

Gas Sources

Helium is used as carrier gas. The gas is regulated by pressure regulator. Pressure is measured at the inlet of the analytical circuit; it is set at about 0.8 kg/cm^2 . At the outlet the flow is set at 25 ml/min. After regulation, the carrier gas is purified if necessary in a scrubbing tube (length 270 mm, diam. $32 \times 28 \text{ mm}$) containing a mixture of "Ascarite"- "Lithasorb" (2:1 v/v, 80 mm long), magnesium perchlorate (80 mm), and "Sicapent" (80 mm). Flow-rate is measured with a "soap film" flowmeter. The gas from the second source is pure electrolytic oxygen, also regulated by a pressure regulator and a flow restrictor. Normally this gas contains as impurity only H_2O (10 ppm); it practically does not require purification. In fact improper use of adsorbents frequently produces unexpected nitrogen blanks.

Oxygen Dispenser Valve

This valve controls the injection of discrete amounts of pure oxygen into the carrier gas stream at the beginning of each analysis. Fig. 2 shows how it functions. In the normal operating position (Fig. 2B) helium flows directly through the valve into the circuit, and oxygen continuously flushes the dosing loop, and vents to the atmosphere. At the beginning of the analysis, the valve is switched from position B to C (Fig. 2). The dosing loop is thus directed into the analytical circuit and the oxygen is carried into the combustion zone by the helium stream. After a preset time, the valve returns to position B. The automatic switch from one position to the other is controlled pneumatically.

A 5-ml dosing loop is used for sample sizes up to 1.0 mg, and for larger sizes a 10-ml loop is used. Increasing the oxygen pressure in the loop (from 0.20 to 1.5 kg/cm^2) allows different amounts of oxygen to be injected without altering the pressure-equilibrium in the system.

The oxygen arrives in the combustion area as a plug, taking about 30 sec. to pass through, and reaching a maximum concentration of 60—70% in the helium.

Automatic Sampler

The sample dispenser acts as a dry storage in helium for weighed samples, after they have been purged from atmospheric contaminants, holding them ready for combustion.

The sampler is mounted on the top of the oxidation reactor, and consists of a container, with a cover and inspection window, and sweeping valve; inside it contains a rotating drum with 24 numbered holes around the edge, in which the sample containers may be placed. An electrically activated pneumatic mechanism is timed to turn the drum in steps of 15° , positioning each hole in turn onto the axis of the reactor, so that the container falls into the reactor by gravity.

Fig. 2A shows the position of the sampler with respect to the circuit when it is purged with helium at 300 ml/min for 2 min. During analysis

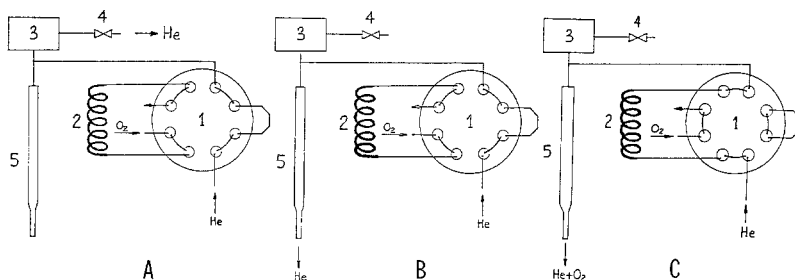


Fig. 2. Disposition of the injection valve in respect to the analytical circuit: (A) sweeping stage, (B) usual position, (C) oxygen injection position
(1) Injection valve, (2) Dosing loop, (3) Sampler, (4) Sweeping valve, (5) Reactor

(Fig. 2B) the carrier gas by passes the sampler, and the samples remain under an atmosphere of helium. They are also cooled by water circulating in the sample support plate.

Oxidation Reactor

The reactor consists of a quartz tube, the size and packing of which are shown in Fig. 3A. The tube is arranged upright so that the samples may be introduced from the top. The vertical position makes the packing more stable, and the tube may be easily removed from above. A quartz crucible is placed in the combustion zone to protect the tube from damage during flash combustion (Fig. 3A) and to collect the spent containers.

The lower part of the tube is tapered in order to avoid dead volume after the packing. The oxidation and reduction reactors are linked, as shown in Fig. 1, by a silver tube (4×2 mm), heated to 120⁰ C and connected to the circuit by Viton O-rings and metal gasket connections.

Reduction Reactor

The reduction reactor consists of a quartz U-tube (Fig. 3B) standing upright, and heated to 640⁰ C. It is loaded from both ends, and packed by means of a vibrator. It should last for 900 analyses (6–7-ml oxygen injection). It is connected to the chromatographic column via a silver tube (4×2 mm), heated to 120⁰ C throughout its length.

Chromatographic Column

A stainless-steel column is used, diameter 6×5 mm, length 3 m, filled and tightly packed with Porapak Q (80–100 mesh) pretreated according to the manufacturer's instructions. After packing, the column is coiled, connected

to the two parts of the circuit and fixed to the heating block. It is then heated to a preselected constant temperature between 120 and 125°C. The filling causes a 0.5 kg/cm² pressure drop, with a flow rate of 25 ml/min.

Detection and Measuring System

The detector used is a conventional catharometer with four WX Rhenium-Tungsten 9225 filaments as sensing elements, (Gow-Mac Instruments Co., Madison, N. J. 07940), assembled in a Wheatstone bridge with a voltage source stabilized at 20 V; the bridge current is 120 mA. It is placed inside a

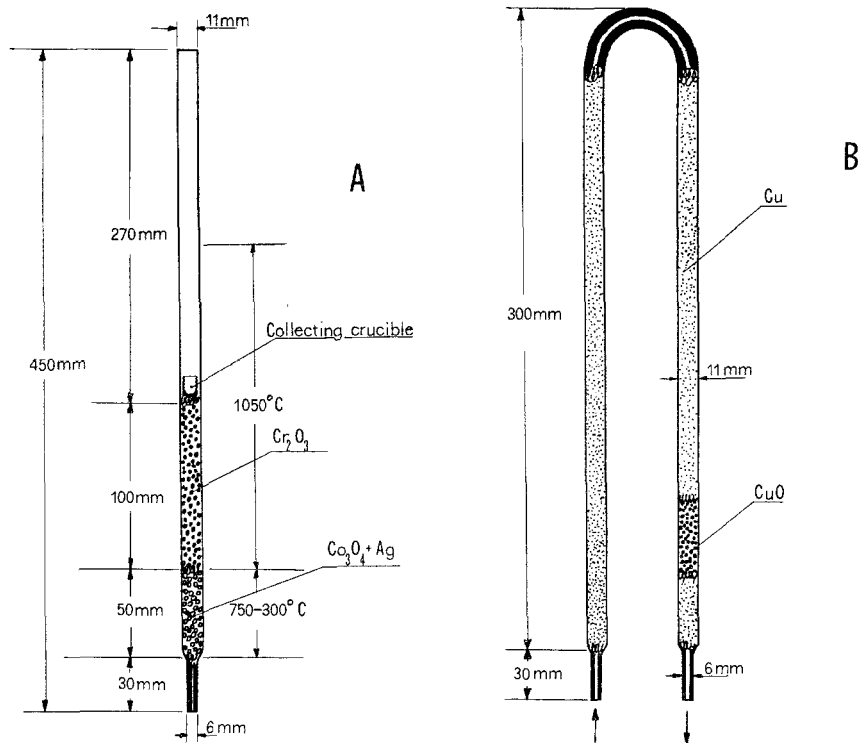


Fig. 3. Combustion train: (A) oxidation reactor, (B) reduction reactor

cylindrical aluminium block, around which the chromatography columns are wound. After 60 min operation, a constant temperature of $120 \pm 0.05^\circ\text{C}$ and a bridge supply voltage constant to $\pm 0.05\text{ mV}$ are reached.

The detector is equipped with an automatic sensitivity switch, which after the N_2 signal has been registered lowers the sensitivity by a factor of 4 for the CO_2 signal and then returns it to the initial value.

The electric signal from the detector feeds the potentiometric recorder and an electronic digital integrator with data print-out, in parallel with the

recorder. The recorder is used essentially for controlling the combustion process and to permit the time control of the successive operations. The electronic integrator is connected directly to the detector bridge without automatic attenuation. The integrator is a simplified voltage-to-frequency converter, in view of the analytical system used. It contains no drift correctors or slope detectors, and no valley sensors, since the baseline is steady and drift-free. There is, however, an automatic zero device. As the integrator receives the signal directly from the detector, errors caused by the recorder such as pen delay, variations in chart speed, and excessive peaks are avoided. On attenuation 8, the integrator speed is 12.000 pulses/minute f. s. Total accuracy is to within 0.1%.

Reagents

Helium R for G. C. Purity 99.998%. SIAD, Bergamo (Italy).

Oxygen. Purity 99.999%. SIAD, Bergamo (Italy).

Al foil for containers, thickness 0.005 mm. C. Erba, Milan.

Sn foil for containers, thickness 0.01 mm. C. Erba, Milan.

"Lithasorb" 16—25 mesh, Fisher, Fair Lawn, N. J., U. S. A.

"Sicapent" 7—16 mesh. Schuchardt, Munich, West Germany.

Cr_2O_3 (25—60 mesh) (available from C. Erba, Milan*). For its preparation, 200 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, analytical grade, are dissolved in 1500 ml of distilled water. The stirred solution is treated slowly with 150 ml of 32% ammonia solution. After precipitation of the hydroxide, the solution is boiled for about 15 min. The precipitate is filtered off on a Gooch crucible and washed several times with distilled water. It is then dried for 12 hr in an oven at 120°C, and heated at 1100°C in an oxygen stream. The dry pulverized reagent is then compressed under 1500 kg/cm² pressure in a tableting machine, broken up, and granulated to 0.7—0.25 mm.

$\text{Co}_3\text{O}_4/\text{Ag}$, 25—60 mesh; prepared according to the literature¹¹. Before use, it is heated in an oxygen stream for 2 hr at 750°C.

Cu, containing Ag, 25—45 mesh. Commercially available CuO is ground and sieved to 0.4—0.7 mm, then 100 g are treated with saturated silver nitrate solution (7.5 ml). The mixture is heated, with stirring, in an evaporating dish until the nitrate completely decomposes. The reagent obtained is reduced in a stream of carbon monoxide at 300°C and then heated 2 hr at 700°C.

Porapak Q, 80—100 mesh. Waters Assoc. Inc., Framingham, Mass., U. S. A. Before use the product is purged for 5 hr at 230°C in a stream of helium.

Procedure

The sample size may be between 0.1 and 3 mg according to analysis requirements. For routine analysis a sample of between 0.5 and 1.0 mg is weighed. In this case the 5-ml oxygen dosing loop

* Patent pending.

is used, and the attenuation values are 8, 32 and 8. An electronic microbalance is used; larger samples may be weighed on a normal microbalance.

Solid samples are weighed into cylindrical containers (height 6 mm, diam. 6 mm), made either of Al (weight 1.8 mg) or Sn (6 mg). The containers are washed with solvent and dried before use. Sn containers should be used for samples containing alkali metals, boron, phosphorus or any substance that does not burn easily. When the substances have been weighed, the containers are closed with tweezers and folded over, then placed in the numbered holes of the sampler drum. Sn containers can be mechanically sealed with pliers. This procedure can be applied to volatile solid samples. Ag capillaries (height 6 mm, diam. 2×1 mm) are used for sampling volatile liquids. The liquid is introduced by means of a microsyringe; then the capillaries are mechanically sealed and weighed. If the weight is constant, perfect sealing has been obtained.

One analytical cycle consists of 23 individual combustions, two or three of which will be of standard compounds. The drum is placed in the sampler, the cover is screwed down, and the sampler body is purged (Fig. 2A). After two minutes the sweeping valve is closed, and the carrier gas enters the analytical train (Fig. 2B). At the circuit inlet, the positive pressure of about 0.8 kg/cm^2 is restored. The carrier-gas flow-rate (25 ml/min) at the outlet of the CHN and reference channels is checked.

The following general steps should then be taken, before starting up the analytical cycle:

- (a) the programmer is set for 7 min analysis time;
- (b) the "sample in delay" timer is set at about 15 sec;
- (c) the integrator autozero is set at about 30 sec before the N_2 peak;
- (d) the auxiliary timers are set for automatic sensitivity switching before and after the CO_2 peak. These times also apply for printing out the integral counts for N_2 and CO_2 . The print-out of the H_2O peak takes place about 1 min after the end of analysis.

The following preliminary operations should also be carried out before each analytical cycle: (I) the detector should be switched on 1 hr before starting analysis; (II) the recorder is switched on (the integrator remains on all the time); (III) the recorder pen is zeroed and the baseline checked at attenuation 1; (IV) the attenuation switch is set on 8; (V) the integrator signal is zeroed to the baseline; (VI) the manual control is switched over to automatic. At this point the

analytical cycle may be started, carrying out 23 combustions automatically. Fig. 4 shows the sequence of events which occurs in each process.

The regularity of combustion is checked on the chromatogram, and the print-out sheet gives the integration values for each process, which are to be introduced into the calculations.

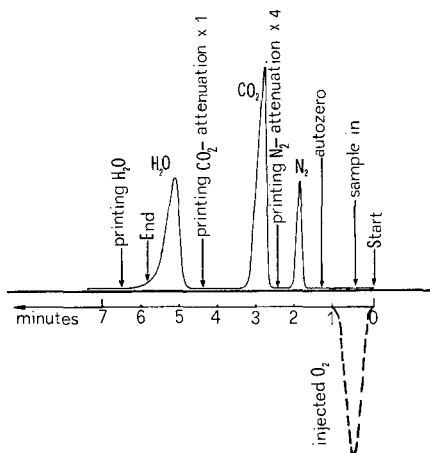


Fig. 4. Events sequence of a single CHN determination

The printed counts (I_x) are multiplied by the calibration factors (f_x) and divided by the sample weight (E) in μg ; then % x is given by

$$\% x = \frac{I_x f_x}{E}$$

The calibration factors (f_x) are determined by combustion of test substances and represents the amount of element in μg corresponding to 100 counts. Correction for blanks is needed only working out the hydrogen content. A typical blank figure is 20 counts, equivalent to 1.4 μg of H_2O .

Study of Optimal Conditions

Combustion

In combustion under dynamic conditions, with use of gas chromatography to separate the combustion gases, unquestionably the samples must be burned as fast as possible. The addition of oxygen

donors is incompatible with this. The literature ^{4,8,12} offers a few good examples of flash combustion. When an organic sample, wrapped in a foil of an oxidizable metal, is introduced in a reactor held at $\geq 1000^{\circ}\text{C}$ and when oxygen is present in sufficient amount, then oxidation of the metal and combustion of the sample occur immediately in a flash of light. The extremely high temperature reached *in situ* ($1700\text{--}1800^{\circ}\text{C}$) stimulates oxidation of any carbonaceous residue.

Ag, Al and Sn foils are suitable for use as containers. Ag foil, 0.01 mm thick, does not, however, produce instant, high-temperature combustion, and in the melted state it still retains small quantities of carbon, because it is not oxidizable. Ag is thus only used in the case of volatile liquids.

At high temperatures, in presence of oxygen, aluminium oxidizes immediately without melting, ensuring perfect flash combustion of the sample. The finest foil should be used so as to consume the minimum amount of oxygen. The thickness which meets these conditions as far as possible, while not making the container too fragile to be handled safely, is 0.005 mm. Since the aluminium does not melt, the inorganic residues of container and sample may still contain in some cases traces of carbon. Sn boats¹³ and mixing the sample with Sn powder¹⁴ have also been described as achieving complete combustion.

We used Sn containers, made with 0.01-mm Sn foil. They give good flash combustions. With Al containers the combustion is immediate; with Sn containers, the combustion is complete a few seconds after the introduction of the container. At first the Sn melts and then oxidizes; simultaneously the organic material is completely burnt. The inorganic residue, when Sn containers are used, does not contain any carbon even if the samples contained alkali metals, boron, phosphorus or silicon. Sn is also useful with low carbon-content substances which do not give flash combustion*.

Flash combustion alone in an oxidizable metal container does not ensure the quantitative oxidation of the organic material. Other authors¹⁵ have observed the formation of CH_4 following flash combustion. We have even noted the formation of carbon particles in an "empty-tube" method.

It is therefore necessary to follow the flash combustion with a high temperature catalytic reaction to ensure quantitative oxidation of the gaseous and solid products.

* We now prefer Sn containers.

Catalytic Oxidation

The greatest drawback of instrumental methods of elemental analysis is the lack of a suitable oxidizing catalyst. CuO, used most frequently, is not a very effective combustion catalyst. It is used because it does not adsorb the combustion gases, an absolute requirement in gas chromatography. A good catalyst for combustion—gas chromatography methods should have the following properties:

- (1) high oxidizing power, even in mixtures of inert gas and oxygen;
- (2) rapid catalytic oxidation;
- (3) chemical and physical stability at high temperature;
- (4) structure free from adsorption sites;
- (5) good mechanical resistance;
- (6) chemically inert towards quartz.

The use of a catalyst layer is necessary to ensure quantitative combustion, to increase the oxidative capacity of the system, and, by avoiding any dead volume after the flash combustion area, to prevent uncontrollable diffusion between helium and combustion gases. This is most important, as diffusion leads to tailing in the chromatographic peaks.

In the search for a suitable catalyst many products have been tried, some already known, some new. The selection was made considering the six requirements above. Only a few of those tried, Co_3O_4 , NiO and Cr_2O_3 , may be considered suitable for combustion—gas chromatography, and even then there are limitations.

Co_3O_4 cannot be used at temperatures above 750°C , and tends to give powder. The oxide mixed with silver¹¹ offers better mechanical resistance.

NiO is an excellent catalyst, suitable for use at high temperatures, almost free from adsorption sites, but either alone or mixed it strongly attacks the quartz tube.

Cr_2O_3 meets four of the requirements very closely, but tends to absorb combustion gases temporarily, and has absolutely no cohesion. Good performance is reported in the literature¹⁶, but its practical application has been extremely limited^{17,18}. This seems to be due to the lack of cohesion, to its supposed deactivation by organic halogens¹⁹ and to the preparation procedure. It was prepared by decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. By this method a mixture of chromium oxides is obtained, which varies in composition and changes its volume on heating.

We use pure Cr_2O_3 obtained by heating chromium hydroxide, precipitated from Cr(III) solutions with ammonia. This oxide is not attacked by halogens or by sulphur oxides.

In order to overcome adsorption and the lack of cohesion, the substance was compressed at high pressure. Pressures around 1500 kg/cm^2 enabled us to obtain a granular preparation, with good mechanical resistance, free from adsorption sites. The surface area, measured by the BET method²⁰, was 5—6 m^2/g . The new reagent has all six requirements of a catalyst for use in a combustion—gas chromatography method.

Oxidizing power, assessed on the basis of the combustion of paraffin, cholesterol, polypropylene, etc., is excellent. The calibration factors show no variation, and no traces of CH_4 are found. Thermal stability is so good that the product may be used without trouble up to temperatures of 1800—1900°C. Cr_2O_3 has a long working life, lasting several months; no damage occurs to the quartz tube provided the reagent is really pure.

The catalytic filling of the tube (Fig. 3A) consists also of a layer of granular Co_3O_4 containing silver. This has proved very efficient in retaining halogens (except fluorine) and sulphur oxides. Moreover the layer of $\text{Co}_3\text{O}_4 + \text{Ag}$, in the position shown, on account of chemiadsorption²¹ temporarily adsorbs the oxygen, releasing it slowly. Consequently the copper in the reduction section is consumed gradually, whereas when Co_3O_4 is not used this occurs rapidly.

Elimination of Unwanted Gases

Cr_2O_3 has no effect on the elimination of halogens and oxides of sulphur. Halogens and oxides of sulphur are chemiadsorbed, by use of $\text{Co}_3\text{O}_4 + \text{Ag}$ as described earlier. We also tried other silver preparations. Ag wool was too unreactive, while Ag on alumina²² produced excessive adsorption phenomena.

To find a reagent that eliminates fluorinated gases and is suitable for use in a method of combustion—gas chromatography, is a difficult task. Reagents containing MgO have proved totally unsuitable because of temporary adsorption of CO_2 and N_2 , and permanent adsorption of H_2O .

The problem has been overcome by making use of the property of the gas chromatographic stationary phase, which binds the fluorine coming from the combustion of fluorinated substances. The actual cause of chemiadsorption of fluorine is presumed to be the addition reaction of fluorine to the terminal double bond of vinyl-ethyl-divinylbenzene.

With the column indicated, the adsorption capacity is over 20 mg of fluorine, after which the polymer, chemically altered, loses its original separation efficiency and has to be replaced.

Any substance containing fluorine may be analysed without trouble. Highly fluorinated substances, such as "Teflon" and "Hos-taflon", show a spurious peak just before the CO_2 peak, which has been attributed²³ to CF_4 . This peak should really be attributed to SiF_4 , and does not interfere with the carbon results (see Table II). This gas disappears when combustion is carried out in the presence of discrete amounts of hydrogen (from LiH) or in a new quartz tube.

Reduction Conditions

The reduction conditions involve the problem of the accuracy of the nitrogen determination. In our experience the accuracy drops remarkably for substances containing only a small proportion of nitrogen, or nitrogen bound as a nitro-group. We have tried to single out the principal causes of error. The incomplete combustion of the substance leads to the formation of carbon residues which retain nitrogen; first of all, then the total oxidation of the organic sample must be achieved.

Another cause which has been suspected for a long time²⁴ is semipermanent adsorption of the nitrogen on copper. This is the reason why, according to Ehrenberger²⁵, with low nitrogen content a correction factor should be applied to the number of counts. Confirmation is provided by the figures in Table I, obtained when using normal copper at 520°C. Deviations, especially as regards the low nitrogen contents, are clear; the values of the table show also that the low hydrogen content values are affected by adsorption of H_2O .

The last cause of error is the inability of copper to reduce quantitatively the bulk of nitrogen oxides from the combustion of nitro-compounds²⁶. Figures for picric acid in Table I confirm this throughout the range of temperatures usually used for copper (500—600°C).

In order to minimize adsorption on copper, a suggestion has been made in the literature⁸ that copper should be used at a temperature of 650°C. This should be one solution to the absorption problem, but causes marked sintering of the copper and gives incomplete reduction of nitrogen oxides*. In an attempt to overcome

* Using normal Cu, nitrogen oxides may be quantitatively reduced by introducing the sample into the reactor before oxygen injection in order to obtain an "autoreduction" reaction²⁷. Picric acid, introduced before oxygen injection, gives accurate nitrogen values (Table I).

these drawbacks, other forms of copper that are considered more active^{28,29} have also been tested. In all cases adsorption increased.

The copper preparation which proved most suitable was copper coated with small quantities of silver, prepared as described earlier. It shows minimal adsorption, has sufficient reducing activity and

Table I.
Carbon, Hydrogen and Nitrogen Results* Obtained by Using Untreated Copper

Compound	% C		% H		% N		Operating conditions
	Calc.	Found	Calc.	Found	Calc.	Found	
Hydrastine	65.78	65.7	5.52	5.7	3.65	2.4	Copper at 520° C
		65.6		5.4		2.3	
Atropine	70.56	70.4	8.01	8.2	4.84	4.0	Copper at 520° C
		70.6		8.2		4.1	
		70.7		8.1		4.0	
1-Chloro-2,4-dinitro benzene	35.58	35.7	1.49	1.1	13.83	13.0	Copper at 520° C
		35.7		1.1		13.2	
Picric acid	31.44	31.3	1.31	1.0	18.34	16.3	Copper at 520° C
		31.4		1.0		16.5	
		31.4		1.1		17.2	
Atropine		70.6		8.1		4.4	Copper at 640° C
		70.6		8.2		4.3	
		70.4		8.1		4.7	
Picric acid		31.2		1.2		17.7	Copper at 640° C
		31.3		1.1		18.0	
		31.4		1.1		17.4	
Picric acid		31.2		1.2		18.3	Copper at 640° C. Introduction of the sample before oxygen injection.
		31.3		1.1		18.4	

* They were calculated using calibration factors obtained by combustion of reference compounds. (nicotinic acid, azobenzene, sulphapyridine).

sinters negligibly. To reduce the sintering further, the copper should be mixed with quartz chips (6:1 v/v). It should be used at temperatures above 600° C, with a layer of CuO in the position indicated in Fig. 3 B.

Other details which should not be overlooked are the materials for the reduction reactor and for the connecting tubings. If the reduction tube is made of metal, it causes tailing in the H₂O peak. Glass loses its shape at pressures above 0.5 kg/cm². Quartz is therefore preferred. The connecting tubing between oxidative and reductive sections consists of chemically inert metal in order to avoid unwanted reactions with oxidation gases, and is heated to avoid water condensation.

Gas-chromatographic Separation

There should be no objective difficulties in the gas chromatographic separation of $N_2-CO_2-H_2O$ mixtures. Difficulties might arise, however, from different combustion rates of the sample, from adsorption and diffusion phenomena and also technically from an unsteady baseline.

Flash combustion at high temperature leads any substance to the same instantaneous mineralization and overcomes problems of different combustion rates. Adsorption is the greatest trouble in gas chromatographic separation, especially because N_2 and CO_2 have similar retention times when the water retention time is made acceptable for practical analysis.

Poor separation of the N_2 and CO_2 decreases the precision and accuracy of the method, even if an electronic integrator is used. The physical interaction between reactor packings and combustion gases is overcome by using reagents which are free from adsorption sites.

Band spreading has been minimized by eliminating dead volume after the combustion section. Maximum care is therefore taken to avoid the copper sintering. The upper free volume of the oxidation tube does not interfere, because of the positive pressure in this region and the dynamic mode of analysis; back-sublimation is also excluded.

An absolutely steady baseline is ensured by introduction of the samples from inside, not outside, the analytical circuit. Sudden volume changes following the flash combustion also have no effect on the baseline because the chromatographic column acts as a buffer volume.

The working temperature for the column has been set at about $120^\circ C$ in order to minimize adsorption, and to shorten the H_2O retention time. The time required for analysis depends strictly on the time needed for separation. For a sample size of about 1 mg, it is advisable to allow at least 7 min analysis time.

The column packing consists of pretreated Porapak Q. The chromatographic columns packed with Porapak are known not to give proportional peak heights. The integrator, however, receiving the signal directly from the detector, prints out the counts proportional to the amounts of effluent gases and peak area. Recording is still necessary, however, to provide a visual indication of the analytical process, show any chemical and operational malfunctions, and to set the right analytical programme.

Table II
Carbon, Hydrogen and Nitrogen Results on Standard and Unusual Compounds

Compound	n	% C			% H			% N		
		X	\bar{x}	S	X	\bar{x}	S	X	\bar{x}	S
Atropine	3	70.56	70.4		8.01	8.1		4.84	4.5	
Nicotinic acid	10	58.53	58.4	0.12	4.09	4.0	0.05	11.38	11.3	0.06
8-Hydroxyquinoline	8	74.47	74.4	0.10	4.86	4.8	0.06	9.65	9.6	0.07
Cyclohexanone-2,4-dinitro phenylhydrazone	22	51.79	51.7	0.09	5.07	5.0	0.04	20.14	20.1	0.11
Picric acid	4	31.44	31.3		1.31	1.2		18.34	18.2	
Pyridine	2	75.92	75.8		6.37	6.4		17.71	17.6	
Naphthalene	2	93.71	93.6		6.29	6.2				
Cholesterol	4	83.87	83.7		11.99	12.0				
Acetonitrile	3	58.51	58.4		7.37	7.4		34.12	34.1	
S-Benzylthiuronium chloride	4	47.40	47.4		5.47	5.4		13.82	13.8	
1-Chloro-2,4-dinitrobenz.	3	35.58	35.5		1.49	1.2		13.83	13.7	
Sulphapyridine	10	52.99	53.0	0.09	4.45	4.4	0.05	16.86	16.8	0.10
Inorganic material ⁺ *	3	0.03	0.02							
Na ₂ CO ₃ [*]	2	11.33	11.2							
5-Chloro-4-hydroxy-3- methoxybenzylisothiurea	4	31.35	31.2		4.09	4.1		8.13	8.1	
phosphate C ₉ H ₁₄ ClN ₂ O ₆ PS [*]										
Teflon ⁺ *	3	24.02	23.7							
Methyldiphenylphosphine oxide, C ₁₃ H ₁₃ PO [*]	3	72.21	72.3		6.06	6.0				
Phenylcarborane C ₈ H ₁₆ B ₁₀ ⁺ *	3	43.59	43.4		7.32	7.3				
Potassium biphthalate [*]	2	47.05	47.1		2.47	2.4				
2,2-Bis(4-hydroxyphenyl) hexafluoropropane [*]	3	53.58	53.5		2.99	2.9				
Nylon [*]	3	63.72	63.5		9.79	9.9		12.39	12.4	
Polyacrilonitrile [*]	1	67.90	68.1		5.70	5.7		26.40	26.0	
Diphenylsilicon- dihydroxide [*]	1	66.63	66.7		5.60	5.6				
Polyethylene [*]	3	85.70	85.4		14.30	14.3				
Unknown fibre ⁺ *	3	?	91.0					?	9.1	
Graphite ⁺ *	3	100.0	99.7							

n = number of runs; X = theoretical%; \bar{x} = average%; S = standard deviation;
* use of Sn containers; ⁺ use of 16—18 ml of oxygen.

Results and Applicability of the Method

Table II shows the results obtained by following the procedure described, with a sample size of 0.5—1.0 mg, using Al or Sn containers. Fig. 5 gives the gas chromatogram for some of the determinations.

The use of Sn containers when the metal acts as cleaving agent for the carbon makes the method applicable to all types of organic substances analysed so far. It is also possible to analyse some inorganic substances (Na_2CO_3 and traces of carbon in minerals) for their carbon content.

The flash combustion method and the possibility of optionally enriching the carrier gas with varied amounts of oxygen, means that refractory substances such as graphite and polymers may be

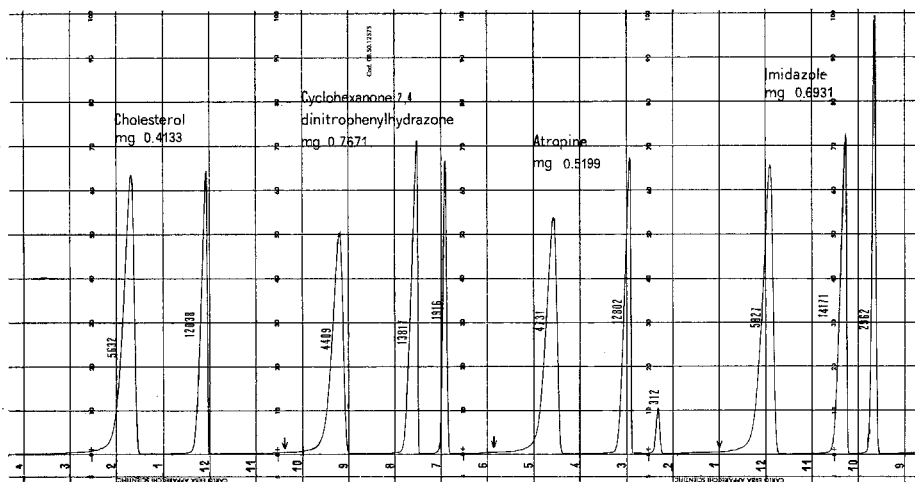


Fig. 5. Analysis chromatograms

quantitatively burned. Except for the massive presence of fluorine, heteroelements cause no trouble.

As regards the sample size, the upper limit in a chromatographic method depends on the following parameters: efficiency of the gas chromatographic column; oxidation capacity of the system; detector response linearity; characteristics of the integrator.

Gas chromatographic separation of the two combustion gases, N_2 and CO_2 , has a limit as to the nitrogen present. The column described, used at 120°C with 25 ml/min carrier-gas flow, may be used with good resolution of the two adjacent peaks of CO_2 and N_2 if not more than $600\ \mu\text{g}$ of N_2 are present. The column efficiency may naturally be improved, but analysis time is lengthened.

If more oxygen is injected, the oxidation capacity of the system can be raised to several mg of sample. The oxidation capacity has been tested on increasing quantities of nitrogen-free test substances

(benzoic acid and phenolphthalein) with injection of proportionally more oxygen.

Fig. 6 shows the linear relation between μg of carbon and the integrator response, up to $3500 \mu\text{g}$ of carbon. Above this limit the response signal becomes anomalous (excess of CO_2 counts). We have not been able to explain the phenomenon. The signal response for

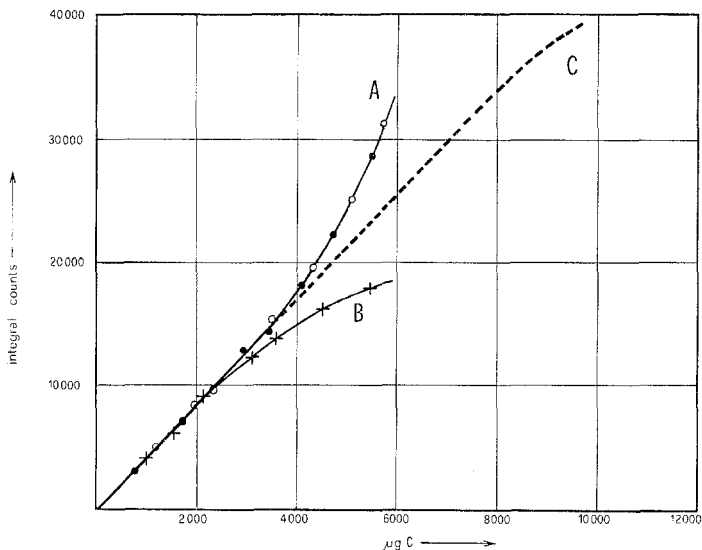


Fig. 6. Response linearity of the system in the case of:
 (A) combustion of CHO standards (\circ benzoic acid, \bullet phenolphthalein);
 (B) combustion of graphite; (C) injection of measured quantities of CO_2

CO_2 coming from the combustion of carbon alone (graphite) is linear up to $2000 \mu\text{g}$ of carbon; then it decreases as expected. The detector response linearity for CO_2/He mixtures has also been tested and found in agreement with the literature³⁰ for binary mixtures. The detector response range is much more broader than the analysis method itself ($2\text{--}8500 \mu\text{g}$ of carbon).

The integrator proved entirely satisfactory for the precise integration of signals coming from the detector. The standard deviations for some test substances, given in Table II, show the precision of the measuring system. The integrator dynamic was checked by combustion of up to 2 mg of test substances, without changing the usual attenuation values (8, 32, 8); the printed value for a peak that was off-scale by a factor of two was still linear and useful for calculation.

The lower limit of sample size for this method is affected by the constancy of gas chromatographic parameters and by the blank

value. Since the system described does not suffer any pressure troubles, the baseline is so steady that even signals at the greatest operational sensitivity values may be recorded and measured.

The size of the blank depends on the purity of the oxygen injected. The periodic injection of oxygen is, as a matter of fact, the only factor altering the composition of the carrier gas since atmospheric contamination in the circuit is excluded. Average blanks with 2, 8, 2 attenuation and injecting 6—7 ml oxygen were: 15 counts for N₂, 5 or 6 counts for CO₂, and 60 counts for H₂O. Table III shows examples of determinations carried out on test substances

Table III. Carbon, Hydrogen, Nitrogen Results for Samples Weighing 100—200 μg *

Compounds	Weight μg	% C		% H		% N	
		Calc.	Found	Calc.	Found	Calc.	Found
Atropine	135.5	70.56	70.5	8.01	7.9	4.84	4.7
	195.7		70.4		8.1		4.8
	112.2		70.4		7.9		4.6
Nicotinic acid	148.8	58.53	58.4	4.09	4.1	11.38	11.5
	183.0		58.7		4.1		11.3
Azobenzene	177.0	79.09	79.0	5.53	5.5	15.38	15.2
	107.3		79.4		5.5		15.3
Cyclohexanone-2,4-dinitrophenyl hydrazone	210.0	51.79	51.5	5.07	4.9	20.14	20.1
	104.8		52.3		5.2		20.4
	104.3		51.9		5.2		20.1
	183.5		51.9		5.0		20.0
Picric acid	132.4	31.44	31.6	1.31	1.2	18.34	18.5
	198.8		31.3		1.2		18.3
	203.0		31.3		1.2		18.4

* Attenuation values 2, 8, 2.

with samples of 0.1—0.2 mg. The greatest deviations refer to low content of nitrogen and hydrogen because of interference from adsorption on copper.

The method may, however, be considered suitable for analysis of organic samples (of average composition) down to 0.1 mg.

Discussion

The use of helium as carrier gas and thermal conductivity measurement methods is no longer a limitation to combustion, as long as the helium is enriched with oxygen and instantaneous combustion is attained, primed by the oxidation of the container.

Flash combustion is more effective than traditional slow combustion. It is even more immediate than Ingram's method of com-

bustion³¹ and involves less oxygen. The combustion is vigorous enough to require no additional catalyst, known to give highly irreproducible blanks.

Because the components of the gas mixture arising from the instantaneous combustion are generated at the same time, a collecting stage is unnecessary and so all its inherent complications are eliminated. The need for a static combustion mode to burn refractory samples is also removed. Flash combustion has one drawback: inorganic residues cannot be determined. Yet the presence of a residue, even in a high amount, does not prevent the determination of carbon.

A logical objection to flash combustion might be that it is difficult to achieve coincidence of the centre of the oxygen plug with introduction of the sample. The timing, however, depends only on the free volume in the combustion tube, and may be checked easily by observing the flash of the metal oxidation. Introduction of the samples slightly ahead of the plug is, however, advisable, especially for nitrocompounds, because when the sample is destroyed with little or no oxygen present, the nitrogen oxides are eliminated by autoreduction. In the procedure described, introducing the sample after a 15-second delay takes advantage of autoreduction in any case, and has no effect on quantitative combustion.

One peculiarity of the method is that both combustion of the sample and elution of the combustion gases are quantitative. This is confirmed by the constancy of the calibration factor, regardless of the composition of the substance analysed.

The only critical point in the method, as far as instrumentation is concerned, is the need for accurate flow control and conditions of thermal equilibrium of the detector. It is no problem maintaining a constant gas flow-rate in the system we have proposed; the problem is to set it always at the same value. The system is however sufficiently gas-tight and the working life of the reactors long enough to ensure the same flow-rate for a few weeks. (The pressure drop due to the column remains constant). Constant temperature levels are ensured by the specially designed heating block, the efficient electronic thermoregulator, and switching on the detector some time before analysis (which can be done without danger, since it works underloaded).

One important point sometimes neglected is the stability of the bridge supply voltage³². To avoid this source of error it is sufficient to use an electronic system which provides maximum stability.

The method can be as fully automated as possible³³, except for weighing of the sample and offers all the attendant advantages. In-

cluding an occasional check-up during the analytical cycle and the final step of writing down the data and calculating the results, CHN data can be obtained on 20 unknown samples in three hours.

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Summary

Study of Carbon, Hydrogen and Nitrogen Determination by Combustion-Gas Chromatography

The method for carbon-hydrogen-nitrogen determination based on dynamic rapid combustion of the sample, gas chromatographic separation and thermal-conductivity measurement of the gases N_2 , CO_2 and H_2O is critically considered and improved. In order to achieve instantaneous combustion of all types of organic compounds, oxidizable metallic containers are used for the sample and dropped in the hot combustion zone while the carrier gas is momentarily enriched with pure oxygen. Flash combustion of the sample is followed by catalytic oxidation on a newly developed active catalyst. This reagent, adsorption-free and thermally resistant, consists of pure chromic oxide, mechanically compressed and granulated. Copper treated with silver is used as reducing reagent. Unwanted gases are eliminated with Co_3O_4 containing silver, and by utilizing the chemisorption properties of the column packing. Measurements are made by integrating and printing the electrical signal. The analytical process is controlled by means of a potentiometric recorder. The increased combustion capacity, the practical absence of blanks and the very extended linearity of response of the detector make possible CHN determination in sample sizes of 0.1—3 mg. Except for sample weighing and calculation of results from the printed integration values, all the operations are automatically controlled by a preset programme.

Zusammenfassung

Das Verfahren zur Bestimmung von C, H und N, das auf der dynamischen Schnellverbrennung der Probe, der gaschromatographischen Trennung und Wärmeleitfähigkeitsmessung der Gase N_2 , CO_2 und H_2O beruht, wurde kritisch überdacht und verbessert. Um die sofortige Verbrennung aller Arten

organischer Verbindungen zu erzielen, wurden die in oxydierbaren Metallbehältern eingewogenen Proben in die heiße Zone des Verbrennungsrohres eingeführt, während gleichzeitig das Transportgas kurzfristig mit Sauerstoff angereichert wurde. Die Verbrennung erfolgt durch katalytische Oxydation an einem neu entwickelten Kontakt, der nicht adsorbiert, hitzebeständig ist und aus reinem, gepreßtem und gekörntem Chromoxid besteht. Versilbertes Kupfer dient als Reduktionsmittel. Störende Gase werden mit silberhaltigem Co_3O_4 sowie durch Chemisorption an der Säulenfüllung entfernt. Die elektrischen Signale werden integriert und ausgedruckt. Der ganze analytische Vorgang wird durch einen Spannungsschreiber kontrolliert. Die erhöhte Verbrennungskapazität, das praktisch vollständige Fehlen eines Blindwertes sowie die weitgehende Linearität der Detektoranzeige erlauben CHN-Bestimmungen in nur 0,1 bis 3 mg Probe. Abgesehen von der Einwaage und der Berechnung der Resultate aus den ausgedruckten Werten verlaufen alle Vorgänge automatisch und programmiert.

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