

CONTINUOUS ELEMENTARY ANALYSIS OF SUBSTANCES SEPARATED BY GAS CHROMATOGRAPHY

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INTRODUCTION

Numerous papers deal with the use of gas chromatography for the elementary analysis of organic compounds. In most cases, the pure substance to be analysed is first decomposed into gaseous products, and these are then separated and determined gas chromatographically¹⁻⁸. The scheme is very similar to classical elementary analysis, except that the final weighing is replaced here by gas chromatographic determination, possibly after some gaseous substances have been converted into a form suitable for such determination.

By contrast, only a few authors⁹⁻¹² have so far attempted elementary analysis of components of mixtures resolved by gas chromatography. The principle of the method is that the substances so separated are converted in a special apparatus into suitable gaseous derivatives, which are then separated on a second chromatographic column. Each component of the original mixture generally gives two products such as CO₂ and H₂.

Even though the accuracy of this determination does not equal that reached in the classical method, the chromatographic technique is sometimes very useful for the identification of unknown components of resolved mixtures.

As mentioned above, two chromatographic columns connected in series have so far been needed for the continuous elementary analysis. This arrangement suffers from the disadvantage that the various components leaving the column in quick succession can be analysed only with great difficulty or, generally, not at all.

The new method proposed here for continuous elementary analysis is basically as follows: The substances leaving the column are first burned to a mixture of CO₂ and H₂, then passed into a first detector which measures both degradation products. The mixture is then led into an absorber which retains carbon dioxide, and the hydrogen is passed into a second detector thus measuring the amount of hydrogen alone. The signals from both detectors are recorded simultaneously on the same chart, and therefore the ratio between the CO₂ peak area and the H₂ peak area gives directly the C/H ratio characteristic of the sample components. Furthermore, the addition of a given amount of a known component to the sample permits one to ascertain whether the latter contains elements other than carbon and hydrogen.

EXPERIMENTAL

The chromatographic separation was carried out by means of a chromatograph with combustion detection¹³ adapted in such a way that a second conductivity detector was also incorporated. The whole arrangement is shown schematically in Fig. 1.

The carrier gas (nitrogen) was led from pressure cylinder 1 through desiccator 2, manostat 3, manometer 4, the reference side of the thermal conductivity cells 7 and 8, into the chromatographic column 6 fitted with a sample injection device 5. The separated components leaving the column were passed into a cylindrical combustion chamber 9, where they were burned and converted into CO_2 and H_2 . This mixture was first led into detector 7, and then through absorber 10—where CO_2 was retained—into the second detector 8, which determined the amount of hydrogen, and then into the flowmeter 11. The recording instrument 12 registered simultaneously the signals from both detectors in such a way that a reversing switch changed the input from one detector to the other every 5 sec.

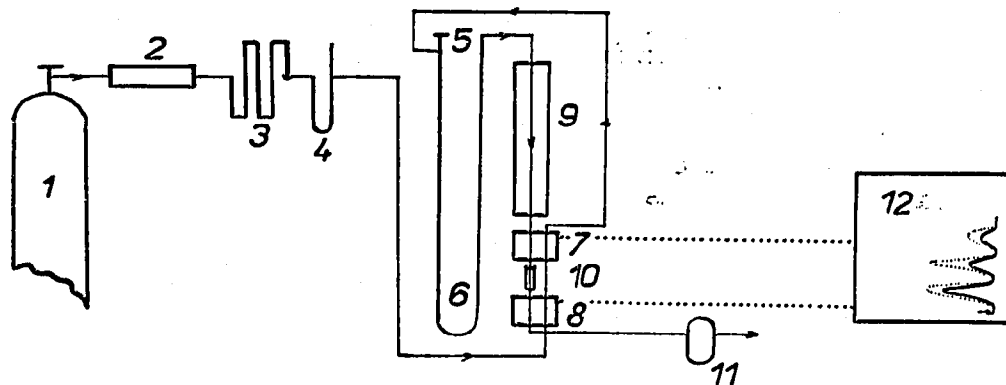


Fig. 1. Schematic diagram of apparatus for C/H determination.

The cylindrical combustion chamber was made of fused quartz and had a length of 34 cm and an internal diameter of 0.5 cm. It was filled with three layers: The first was a cupric oxide layer, the second silver on pumice support¹³, and the third cast iron filings. The best temperatures for these zones were 820, 500, and 620°, respectively.

The absorber 10 between detectors 7 and 8 was a 10 cm long glass tube packing with a layer of asbestos treated with NaOH, the packing being sandwiched in between layers of magnesium perchlorate.

The recorder was of the Honeywell-Brown type, with a range of 1 mV and a quick-response (1/2 sec) pen. The alternation of the two detector signals was ensured by an ordinary time switch.

The thermal conductivity detectors were supplied from the same source, which was a 6 V stabilizer. Owing to its small plate resistance, the same battery could not be used to feed both detectors at the same time.

The sample size varies between 0.01 and 0.08 μl , according to the number of components and their relative concentrations in the mixture. The column was 140 cm long, with a suitable packing, and was heated to the appropriate temperature. The

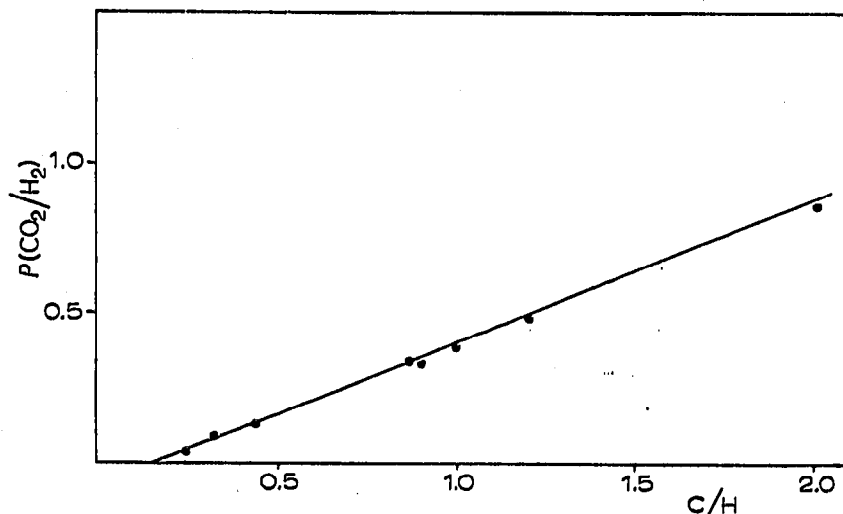


Fig. 2. Calibration curve.

flow rate of carrier nitrogen was 2.0 l/h, and we used samples measuring 0.03–0.07 μ l.

The calibration curve was obtained by determining the C/H ratio for a number of known compounds with different C/H ratios (see Fig. 2). It was found necessary to carry out the analysis at the same detector sensitivity as that used for the recording of the calibration curve.

The following formula was used to calculate the amount of "foreign" elements, *i.e.* elements other than carbon and hydrogen:

$$x \% = \frac{100 \left(\frac{G \cdot K_s}{G_s \cdot K} - \frac{P}{P_s} \right)}{\frac{G \cdot K_s}{G_s \cdot K}}$$

where:

x % = amount of foreign element, %

G = amount of unknown substance, g

G_s = amount of internal standard, g

P = hydrogen peak area for the unknown substance

P_s = hydrogen peak area for the standard

K = $C \times 12 + 10$ (C is the number of carbon atoms in the unknown substance)

K_s = $C_s \times 12 + 10$ (C_s is the number of carbon atoms in the standard).

RESULTS AND DISCUSSION

The results obtained are listed in Table I. Statistical processing of the data for 135 determinations shows that the reproducibility of the method is $s = \pm 5.35$ %, the error being $s = \pm 6.1$ %. This accuracy clearly does not satisfy the requirements placed on elementary analysis. However, we are concerned here with identification of substances, and for this purpose, the results are entirely satisfactory. It can be seen from Table I that the error is somewhat higher for compounds containing oxygen. This is because the same column (RYSORB BLK + 20 % methylphenylsilicone oil) was

TABLE I
C/H RATIO DETERMINATION

Substance	Number of determinations	C/H ratio		ΔC
		Theory	Found	
Benzene	19	1.00/1.00	1.01/1.00	+ 0.010
Toluene	34	0.875/1.00	0.881/1.00	+ 0.006
<i>p</i> -Xylene	25	0.80/1.00	0.815/1.00	+ 0.015
<i>o</i> -Xylene	2	0.80/1.00	0.795/1.00	- 0.005
Chlorobenzene	3	1.20/1.00	1.173/1.00	- 0.027
Cyclohexane	3	0.50/1.00	0.477/1.00	- 0.023
Ethyl acetate	8	0.50/1.00	0.485/1.00	- 0.015
Butanol	1	0.40/1.00	0.460/1.00	+ 0.060
Propanol	2	0.37/1.00	0.430/1.00	+ 0.055
Methanol	1	0.25/1.00	0.270/1.00	+ 0.020
Trichloroethylene	5	2.00/1.00	1.920/1.00	- 0.080
1,3,5-Trimethylbenzene	2	0.75/1.00	0.675/1.00	- 0.075
α -Methylstyrene	5	0.90/1.00	0.896/1.00	- 0.004
Ethylbenzene	6	0.80/1.00	0.758/1.00	- 0.042
Cumene	4	0.75/1.00	0.688/1.00	- 0.062
Chloroform	3	1.00/1.00	1.051/1.00	+ 0.051
Hexane	1	0.43/1.00	0.400/1.00	- 0.030
Octane	3	0.44/1.00	0.523/1.00	+ 0.083

used for all the determinations, which undoubtedly was not equally suitable for all of them. Thus, the separation was not always complete, so that the accuracy of evaluating the resulting peaks decreased.

As regards chromatographic recording, each substance in the mixture gives rise to a peak for ($\text{CO}_2 + \text{H}_2$) and another for hydrogen alone. By subtracting the area of the second peak from that of the first, we obtain the amount of carbon dioxide. Peaks of a convenient size are obtained by adjusting the sensitivity of the two detectors. It is advisable not to alter the conditions in further determinations, since otherwise the contact resistance of the switch might change, and this would modify the results. To ensure that the conditions remained unchanged, we introduced some known substance in the system before the series of determinations.

The recorder gives two broken-line curves, since the time switch interrupts about every 5 sec the signals of one detector to receive signals from the other. Either an ordinary time switch or a mechanical device may be used for alternating the detector signals. The time switch actuates a change-over relay, which must have the lowest possible contact resistance.

The charts were evaluated planimetrically. The hydrogen peak was distinguished from the carbon dioxide peak not only by size, but also by a slight increase in the elution time. This lag corresponded to the time needed for the carrier gas to flow from one thermal conductivity detector to the other. Instead of the present recording system, one may clearly use a two-stage recorder or two recorders, though the latter technique is uneconomic.

The combustion tube, where substances are burned and water is converted into hydrogen, contains not only a CuO zone and an iron zone, but also a layer of silver on pumice support. This is added in order to retain halogens and sulphur-containing substances. The temperature of each zone is an important point. As has been found

earlier¹⁴, the most suitable temperature for the CuO layer is 800–820°. On the other hand, the iron zone must be kept at 520°, since at higher temperatures the carbon dioxide coming from the first layer is reduced to carbon monoxide. The amount of CO increases with increasing temperature of this layer⁹. A tube filled with I₂O₅ was therefore connected by CACACE⁹ to the combustion chamber. However, so as not to complicate the apparatus, we did not use such an I₂O₅ layer. We assumed furthermore that, when the conditions are kept constant, the amount of CO formed has roughly the same low value not significantly affecting the results. Moreover, the difference between the thermal conductivity of nitrogen and that of carbon monoxide is very small ($N_2 = 5.81$, $CO = 5.37$, $H_2 = 41.6$, $CO_2 = 3.52$ cal/cm·sec. at 0°)⁹. A large amount of CO is undesirable chiefly because it is not retained by the NaOH-treated asbestos absorber. Accordingly, the difference in the areas of the two peaks is reduced, even though the C/H change is not changed basically. Magnesium perchlorate was used to trap any water that may be present.

TABLE II
DETECTION OF ATOMS OTHER THAN C AND H

Substance	Standard used	Other atom %	
		Theory	Found
Ethyl acetate	<i>p</i> -Xylene	36.5	38.6
Ethyl acetate	Toluene	36.5	43.5
Chloroform	Toluene	89.09	88.5
<i>p</i> -Xylene	Toluene	0.0	—2.1
Toluene	<i>p</i> -Xylene	0.0	—3.4
Benzene	Toluene	0.0	3.4

As mentioned before, this method of the continuous determination of the C/H ratio is very useful for the identification of unknown mixtures. As regards the determination of elements other than carbon and hydrogen, we applied to single substances the method based on the addition of a weighed amount of a known compound to a weighed sample. The formula given in the Experimental part was then used to calculate the amount of "foreign" elements. The results shown in Table II indicate that it is possible to determine other elements, though not very accurately.

The boiling point and the chemical properties of the internal standard are of utmost importance. Thus, it has been found that, when a syringe is used to inject a sample and a standard differing in polarity and boiling point, the more volatile substance suffers partial evaporation when the needle of the syringe approaches the hot injection device. This evaporation leads to a systematic error, which may be eliminated by using a glass capillary. The resulting accuracy is satisfactory for identification purposes for the introduction of the sample.

Finally, it should be stressed that another advantage of the present method lies in the fact that it can be used to determine the C/H ratio not only in pure substances, but also for mixtures which are resolved chromatographically. The present method is therefore a useful complement to other techniques of identification.

SUMMARY

A method was devised for the continuous determination of the C/H ratio for identification purposes, the method being based on gas chromatography. The components leaving the gas chromatograph are burned to CO₂ and H₂O in a special combustion chamber, and water is converted into hydrogen. The amount of combined CO₂ and H₂ is recorded by one detector, then CO₂ is fixed in an absorber, and the amount of hydrogen alone is determined by a second detector.

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