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A New Gas-Chromatograghic Method of Organic Elemental Analysis*

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가스크로마토그래피에 依한 微量元素分析

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要 約

微量元素分析用 燃燒爐 內에서 內部酸化劑(酸化銀과 二酸化 망간의 混合物)와 함께 有機試料를 헬륨 氣流下에서 燃燒시키고 發生한 물은 칼슘카바이드管에 通하여 아세틸렌으로 變換시킨다. 二酸化炭素와 아세틸렌을 molecular sieve 5A 管에 室溫에서 吸着시킨 후 340°C까지 溫度·프로그램法으로 脫着시켜 실리카겔管을 通하여 分別流出시키고 熱傳導式 檢知器로 CO_2와 C_2H_2를 定量하는 方法을 發展시켰다.

벤조酸을 標準物質로 하여 作成한 檢量線을 使用하여 各種 有機試料中의 炭素및 水素含量을 分析한 結果 平均誤差가 炭素의 경우 ±0.5%, 水素인 경우 ±0.33% 이었다.

Abstract

A new gas-chromatographic method for determining carbon and hydrogen in organic compounds has been developed.

After sample combustion was performed in a regular analytical combustion tube with an internal oxidant (a mixture of silver oxide and manganese dioxide) under a helium flow, the water produced was converted to acetylene by passing through a calcium carbide tube. The carbon dioxide and acetylene were trapped by a molecular sieve 5A column at room temperature. The trapped gases were released under programmed temperature raise up to 340°C and the released gases were passed through a silica gel column.

The adsorption of CO_2 and C_2H_2 in the molecular sieve 5A trapping column were found to be quantitative

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and the silica gel column showed an excellent resolution of CO_2 and C_2H_2 for analytical purpose.

The analytical results for various known compounds based on the out-put of the thermal conductivity cell calibrated for the amounts of carbon and hydrogen contents in benzoic acid, showed average errors ±0.5% and ±0.33% for carbon and hydrogen, respectively.

Introduction

Since gas-chromatographic technique was introduced into the micro organic elemental analysis, a major problem has been the trapping of gaseous products and instant injection of the trapped gases into the separation column.

Duswalt and Brandt[1], and others[2,3] made use of liquid nitrogen trap whereas Nightingale and Walker[4], and Parsons, Pennington and Walker[5] developed a rapid combustion method using high frequency induction furnace to eliminate the liquid nitrogen trap.

In the present work, a convenient and efficient trapping system has been developed by adopting a double column gas-chromatographic technique; one column for trapping and the other for resolution.

Experimental

Apparatus and materials;

The complete system is shown schematically in Fig. 1. The combustion system of Shimazu-UM-2 micro analytical apparatus was used with some modifications of combustion tube packing as shown in Fig. 2.

A U-shaped stainless steel column of 1/4in. diameter and 2 feet long packed with Linde molecular sieve 5 A (45~60 mesh) activated at 360°C for 24 hours, which was mounted in a manual temperature programming system of Hevi-Duty electric furnace controlled by a variac, was used for trapping purpose.

A stainless steel column of 1/4 in. diameter and 3 feet long packed with silica gel (45~60 mesh) connected to the trapping column was installed in Beckman GC-2 model gas-chromatograph with thermal conductivity cell.

A micro absorption cylinder of Shimazu-UM-2 apparatus, packed with calcium carbide(42—60 mesh) connected to the combustion tube, was used for generation of acetylene from the water produced in the combustion tube.

Helium was used as carrier gas.

All reagents of analytical grade used were obtained from commercial sources.

As internal oxidant, the mixture of silver oxide and manganese dioxide supplied from F & M Scientific Corp. with the apparatus, "Carbon, Hydrogen and Nitrogen Analyzer Model 180."

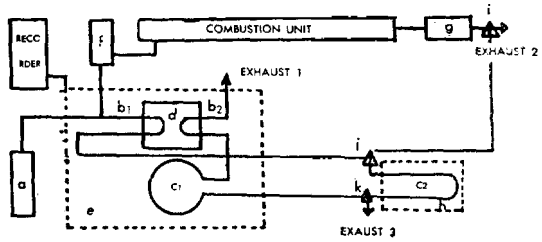

Fig.1. Schematic diagram of complete system for determination of hydrogen and carbon.

a. Helium supply
b_1. Reference branch
b_2. Sensing branch
c_1. Silica gel column
c_2. Molecular sieve 5A column
d. Detector(Thermal conductivity cell)
e. Gas-chromatographic compartment
f. Carrier gas purifier
g. Calcium carbide tube
h. Temperature programmer
i. j. k. Three-way stopcocks

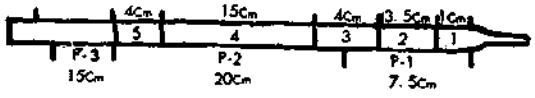

Fig. 2. Combustion tube packing.

1. 3. 5. Silver wires
2. Lead peroxide
4. Cupric oxide
P-1. Heating mortar
P-2. Stationary furnace
P-3. Combusting furnace

Procedure;

The gas-chromatographic unit is warmed up to 130°C with three-way stopcocks *i*, *j* and *k* adjusted so that helium flows throgh combustion tube and trapping column to exhaust 3. The combustion tube is now

warmed up to a steady state; the stationary furnace compartment is kept at 750°C and heating mortar compartment at 210°C

Flow rate of carrier gas is kept at 6ml/min. by means of the internal regulator built in Beckman GC-2.

The sample weighed in a platinum boat and covered with enough amount of the internal oxidant is inserted into the combustion tube with the stopcock *j* turned slightly so that no gas can flow through it; the trapping column is disconnected from the combustion line. After insertion of sample, the opening of the combstion tube is stoppered. Then, with stopcock *j* turned back to the original position, the combustion procedures are carried out in usual manner except for passing helium gas instead of air.

The helium gas flow carries the carbon dioxide and water vapor produced in the combustion tube through the calcium carbide tube *g*, where water is converted to acetylene. The carbon and acetylene are then trapped in the trapping column C_2 which is kept at ambient temperature.

After compeletion of combustion, the combustion line is disconnected from the trapping system and trapping column C_2 is flushed by helium into the resolving column C_1 by changing the flow rate to 40 ml/min. Gas-chromatograph is now turned on and sensitivity is set to Attenuation No. 50 for CO_2 peak. The temperature of the trapping column is raised at 30°C/min. up to 340°C by keeping the furnace supply at 120 volts. When reached 340°C, the trappingcolu mn temperature is kept constant by lowering thevolt age to 70 volts.

In the mean time, when CO_2 peak is completed the Attenuation is changed to No. 10 to enlarge the C_2H_2 peak.

The area of each peak is measured by means of disk integrator.

Calibration curve;

In order to calibrate the areas of carbon dioxide and acetylene peaks to the amounts of carbon and hydrogen, respectively, a series of determinations of carbon and hydrogen in benzoic acid has been carried out and the result is shown in Fig. 3.

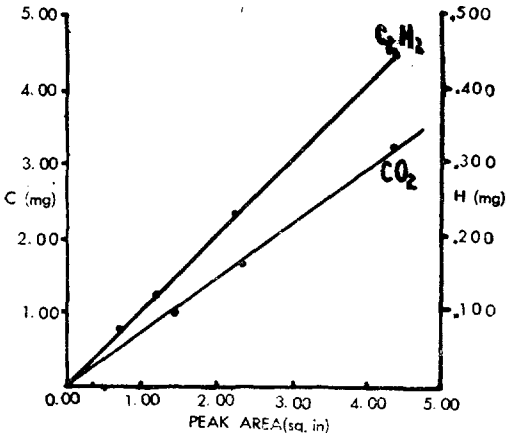

Fig.3. Calibration curves of benzoic acid.
Column; 3 ft. silica gel col.: Flow rate; 40 ml/min.: Column temperature; 130°C: Temperature program 30°C/min.: Chart speed; 1.27 cm/min. Sensitivity; Attenuation No. 50 for CO_2 and No. 10 for C_2H_2. (Sensitivity of C_2H_2 is increased 5 times.)

Results and Discussion

Benzoic acid, ethyl acetoacetate, urea, n-caproic acid and malonic acid were analyzed for carbon and hydrogen using the calibration curve shown in Fig. 3 and the results are summarized in Table. 1.

The average absolute error for carbon is ±0.5%, and for hydrogen is ±0.33%. Data for benzoic acid

Table 1. Determination of carbon and hydrogen.

	Sample weight(mg)	Carbon content(%)			Hydrogen content(%)		
		Found	Calc.	Error	Found	Calc.	Error
Ethyl acetoacetate	4.550	55.7	55.4	+0.3	7.76	7.75	+0.01
	3.104	56.7	55.4	+1.3	7.51	7.75	−0.24
n-Caproic acid	4.988	62.2	62.0	+0.2	10.8	10.4	+0.4
Malonic acid	4.300	34.6	34.6	0.0	4.50	3.88	+0.62
	5.396	34.0	34.6	−0.6	2.98	3.88	−0.90
Urea	5.236	20.4	20.0	+0.4	6.84	6.71	+0.13
	5.158	19.2	20.0	−0.8	6.73	6.71	+0.02
		Aver. error ±0.5%			Aver. error ±0.33%		

are listed in Table 2.

Table 2. Determination of carbon and hydrogen in benzoic acid.

Sample weight(mg)	Carbon content(%) Found	Calc.	Error	Hydrogen content(%) Found	Calc.	Error
1.562	69.7	68.8	+0.9	5.31	4.95	+0.36
2.550	68.8	68.8	0.0	4.95	4.95	0.00
3.158	68.7	68.8	−0.1	4.63	4.95	−0.32
4.850	68.6	68.8	−0.2	4.93	4.95	−0.02
	Aver. error ±0.3%			Aver. error ±0.17%		

It has been confirmed that carbon dioxide is quantitatively adsorbed on molecular sieve 5 A at room temperature and released at 275°C as reported.[6,7] Furthermore, it has been found in the present work that acetylene is quantitatively adsorbed on molecular sieve 5 A at room temperature and released at 285°C. Therefore the authors consider that molecular sieve 5A is suitable for the trapping of acetylene, too. However the peak area of acetylene obtained from molecular sieve column was too small to be evaluated as compared to that of carbon dioxide, which can be anticipated, since acetylene has lower molecular weight, and its retention time in the silica gel column is longer than that of carbon dioxide, and the molar ratio of H_2 : C is usually smaller than unity. Therefore, the elution of acetylene had to be performed with increased detector sensitivity. The typical chromatogram is shown in Fig. 4. The retention time difference of the two components is six minutes, so that the increase of detector sensitivity during the elution can be done without causing significant error.

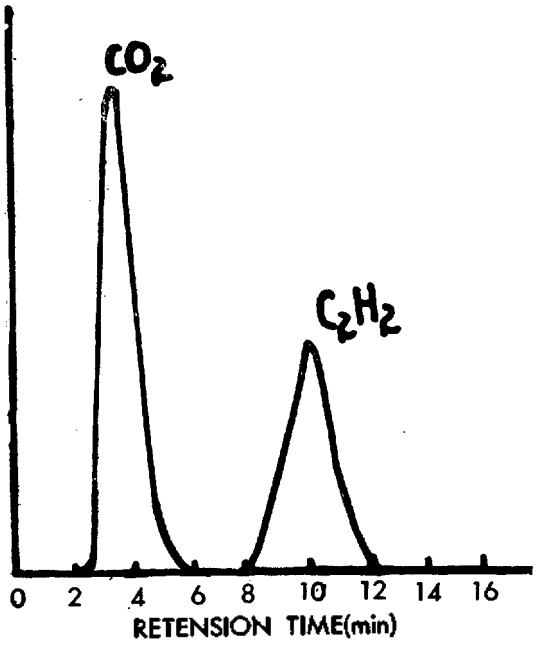

Fig. 4. Typical chromatogram.

The combustion was repeated with several internal oxidants in order to find the best reagents for a complete and consistant combustion. The use of cupric oxide gave incomplete combustion and inconsistant result. The best result was obtained when the mixture of silver oxide and manganese dioxide was used.

Various organic substrates were studied for the column materials. Hexamethylenephosphoamide, apiezon and flexol gave such poor resolved peaks that those could not be used for analytical purpose. Silica gel which has been used for a gas-solid partitionar, was able to give a relatively sharp elution and resolved peaks at 130°C.

In conclusion the present method offers a new means of the gas-chromatographic elemental analysis of organic compounds.

The precision of the method is comparable to that of the present existing micro techniques.

The time required for analysis in series was about 30 minutes.

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