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Pyrolytic Sulfurization Gas Chromatography. XVI. Pyrolytic Sulfurization Reaction at Atmospheric Pressure and Its Application to the Identification of Carbon, Hydrogen, Oxygen, and Nitrogen in Organic Components

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A new method by which the component elements: C, H, O, and N, in an organic compound can be simply, rapidly, and economically identified was established on the basis of the reaction of an organic compound with sulfur at atmospheric pressure. The apparatus for this method consists of two gas chromatographs and an original reactor for reacting an organic compound with sulfur vapor. One component separated from a given mixture by the use of one gas chromatograph was made to react with sulfur vapor in the original reactor and then the reaction products were analyzed by the use of the other gas chromatograph. The reaction products were restricted to seven kinds of compounds irrespective of the chemical structure of the target component. According to this method, the component elements: C, H, O, and N, in an organic compound could be easily identified by the reaction products within 20 min with a detection limit of a few pmol.

It is well known that gas chromatography-mass spectrometry(GC-MS) and atomic emission spectrometry(AES) using inductively coupled plasma (ICP) or microwave induced plasma(MIP) excitation are useful tools for identifying or determining component elements in a sample. However, the component elements in a sample cannot be easily identified or determined by means of GC-MS, though GC-MS can in principle clarify the chemical structure of a compound which can vaporize at relatively low temperature by its fragmentation. But complicated data analysis is required to clarify the chemical structure of the compound. On the other hand, though the component elements in a sample are easily identified by means of ICP- or MIP-AES, the applicable elements are restricted to heavy elements, such as metal elements. Few reports concerning the identification of light elements such as C, H, O, and N are available.[1–3] Moreover, both mass spectrometry and AES have the following disadvantages: 1) The apparatus is very expensive, 2) the system is very complicated, and 3) data analysis is very troublesome. Accordingly, it is now difficult to identify simply or to determine the component elements in an organic compound by means of instrumental analysis. Therefore, a new method by which the light elements such as C, H, O, and N in an organic compound can be simply, rapidly, and economically identified was investigated and successfully established. This method is based on the reaction of an organic compound with sulfur vapor at atmospheric pressure in the flow of sulfur vapor: A target component separated from a given mixture by gas chromatography is introduced to the reactor and is made to react with sulfur vapor, and then the resulting products are analyzed by gas chromatography. The apparatus used for this method consists of two gas chromatographs and an original reactor, in which a target component reacts with sulfur. The apparatus is set up by linking one gas chromatograph, the pyrolytic sulfurization reactor, and the other gas chromatograph in series in that order. This method will therefore be called "gas chromatograph-pyrolytic sulfurization reactor-gas chromatography (GC-PSR-GC)". By using GC-PSR-GC under the optimum conditions, carbon in an organic compound is mainly converted to carbon disulfide (CS_2) and/or carbonyl sulfide (COS), hydrogen to hydrogen sulfide (H_2S), oxygen to COS, and nitrogen to hydrogen cyanide (HCN). Therefore, the component elements, C, H, O, and N, in a target component can be successfully identified by observing four kinds of reaction products: CS_2, COS, H_2S, and HCN. The time necessary for an analysis by GC-PSR-GC is about 20 min.

Experimental

Reagents. The sulfur used as a reaction agant with a sample was obtained by purifying[4] commercially available sulfur (chemical pure). The organic compounds used as standard samples were of reagent grade; their purities were confirmed by gas chromatography. Helium as a carrier gas was purified in the present apparatus by passing through a stainless steel column(3 cm i.d. and 18 cm long) packed

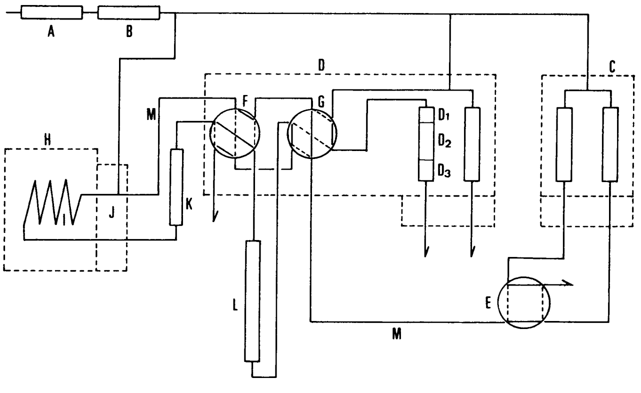

Fig. 1. Schematic flow diagram of the system.
A: Molecular sieve 5A column, B: copper column, C: gas chromatograph-I, D: gas chromatograph-II, D_1: Chromosorb 104 column, D_2: Porapak QS column, D_2: Deactigel column, E: four-way cock, F and G: six-way cocks, H: electric furnace, I: reaction tube, J: quartz-made apparatus, K: sulfur trap, L: trap column, and M: stainless steel tube.

with Molecular Sieve 5A (60—80 mesh) and a copper column (8 mm i.d. and 35 cm long) packed with sponge granular copper(12—25 mesh) heated at 380 °C.

Apparatus. The apparatus constructed for this study is schematically illustrated in Fig. 1. This apparatus consists of the following four sections: 1) Introduction section of a target component, 2) generation and condensation section of sulfur vapor as a reaction agent, 3) reaction section of the component with sulfur vapor, and 4) analysis section of the reaction products. The sections are constructed in the following detailed manners:

Section 1: A gas chromatograph(Shimadzu GC-4CPT)-I (GC-I) (C) mounted with a four-way cock(E) held at 180 °C was used for the introduction of a target component to the pyrolytic sulfurization. GC-I was operated under the optimum conditions for a sample, except that the flow rate of He as a carrier gas was set at 11 cm^3/min. All the stainless steel tubing (1.5 mm o.d. and 1.0 mm i.d.) (M) used to introduce a target component to the reactor were held at 180 °C, so as to prevent the condensation of the component in the tube.

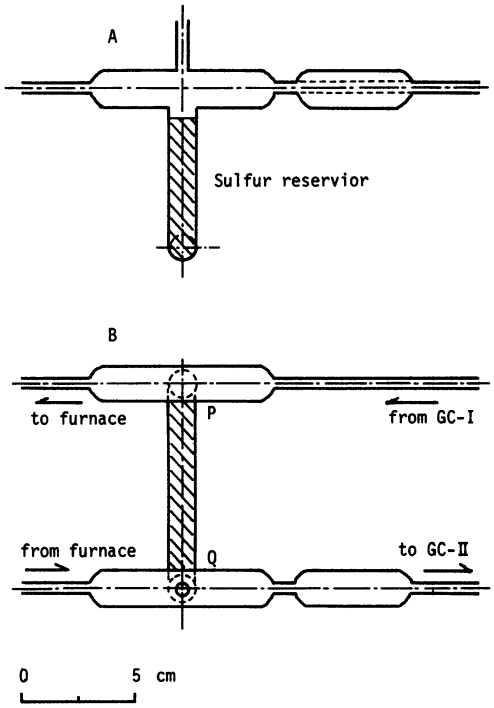

Fig. 2. The apparatus for supplying and recovering sulfur vapor.
A: Front view and B: plain.

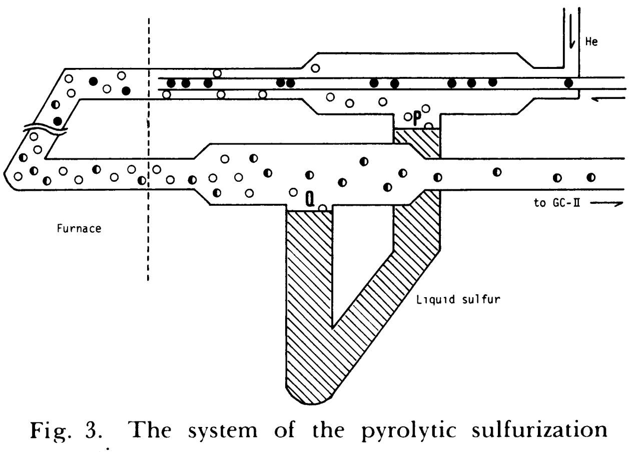

Fig. 3. The system of the pyrolytic sulfurization reaction.
○: Sulfur, ●: sample, and ◐: products.

Section 2: The quartz-made apparatus (J) by which sulfur vapor could be supplied and recovered was designed and constructed; this is shown in Fig. 2. Sulfur vapor was generated from the position P in Fig. 2 by heating it at 350 °C and was carried into the reaction section by He at a flow rate of 4 cm^3/min; then the sulfur vapor was condensed at the position Q held at 150 °C. Sulfur trap column (4 mm i.d., 6 mm o.d., and 10 cm long) (K) packed with quartz wool was connected with this apparatus for completely eliminating sulfur mist.

Section 3: A spiral quartz tube(2.5 mm i.d., 4 mm o.d., and 5 m long) (I) was used as a reaction tube by placing it in a electric furnace (Seiwa Riko Co. Ltd., FDH-15) heated at 900 °C.

Section 4: A gas chromatograph (Shimadzu GC-4CPT)-II (GC-II) (D) mounted with two six-way cocks (F and G) and a stainless steel column (3 mm i.d., 4 mm o.d., and 50 cm long) (L) for trapping the reaction products was used for analyzing the reaction products; the trap column was packed with Silica gel (60—80 mesh). The reaction products could be trapped in this column at room temperature and released from this column by heating it to 250 °C. GC-II was operated under the following conditions: A 0.25 m stainless steel column D_1 was packed with Chromosorb 104 (80—100 mesh), a 1.75 m stainless steel column D_2 with Porapak QS (80—100 mesh), and a 0.2 m stainless steel column D_3 with Deactigel (60—80 mesh) were used by linking them in series in that order. The column temperature was programmed between 80 and 185 °C at the rate of 20 °C/min. The flow rate of He carrier gas was 30 cm^3/min at room temperature.

The system for the pyrolytic sulfurization reaction between a target component and sulfur vapor by the use of the present apparatus is illustrated in Fig. 3. The component gas and sulfur vapor were mixed just before the entrance of the furnace and then the mixture components were made to react in the furnace. The reaction products thus obtained and the excessive sulfur over the pyrolytic sulfurization reaction were separated at the position of the condenser (Fig. 3, Q) by condensing the excessive sulfur vapor to liquid sulfur, and only the reaction products were introduced to the analysis system by GC-II. Therefore, this system for supplying and recovering sulfur makes it possible to minimize the sulfur consumption necessary for the analysis and allows the excessive sulfur to be reused for the next analyses.

Procedure. Several decimilligrams of a sample, either a single compound or a mixture, was injected into GC-I by the use of a microsyringe and the elution behavior of the sample was monitored by the thermal conductivity detector installed in GC-I. The target peak of the sample to be analyzed was introduced to the reactor of pyrolytic sulfurization by operating the four-way cock E, and other compounds, if present, were sent from the exit at the same time. The target component was mixed with sulfur vapor generated from a sulfur generator just before the furnace. Then their mixture were subjected to react for about 1 min during the passage through the reaction tube heated at 900 °C by the electric furnace. The products thus obtained were separated from the excessive sulfur and only the products were trapped by the trap column L at room temperature for 2.5 min after the elution from GC-I. The reaction products trapped were released from the trap column and introduced to GC-II by operating two six-way cocks (F and G) and by heating the trap column rapidly to 250 °C, followed by analysis by the use of GC-II. The peak areas of the products on the gas chromatogram of GC-II were read out by the use of the integrator (Shimadzu digital integrator E1A). By the use of the chromatogram thus obtained, the component elements C, H, O, and N, in the target component were qualitatively identified.

Results and Discussion

Optimization of the Reaction Conditions between a Sample and Sulfur. Flow rate of carrier gas, He, for supplying a target component to the reactor was set at 11 cm^3/min, and that for supplying sulfur vapor was set at 4 cm^3/min, based on the design of the apparatus. In these experimental conditions, vaporizing temperature for supplying the sufficient sulfur necessary for the pyrolytic sulfurization of the component was examined by the use of 1 μl of toluene, which did not seem to be so reactive with sulfur (Fig. 4). Figure 4 indicates that vaporizing temperature of sulfur has to be held over about 350 °C. Therefore, the vaporizing temperature of sulfur was chosen at 350 °C as its optimum condition.

The reaction temperature of the component with sulfur vapor in the electric furnace was also examined by the use of 1 μl of toluene as a standard sample; the effects of the furnace temperature on the amount of products are shown in Fig. 5. The reaction temperature has to be held over about 850 °C. Moreover, COS as a blank was produced at a temperature of over 1100 °C; this may be attributed to the fact that carbon in the component reacted with the internal surface of the reaction tube.[5] Therefore, the reaction temperature was chosen at 900 °C as its optimum condition.

Trap Time of the Reaction Products. The products from the reaction between a target component and sulfur were trapped by the stainless steel column packed with silica gel. The time necessary for trapping the products was examined; the effects of trap time on the amount of the products are shown in Fig. 6. Figure 6 indicates that a trap time over 15 min is required to trap quantitatively all the products from a target component. In the present conditions, a small

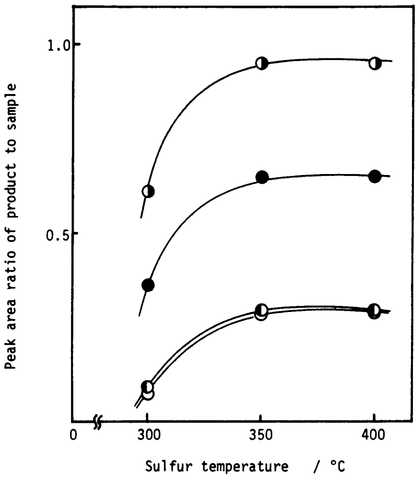

Fig. 4. Effect of the sulfur temperature on the amount of products.
○: H_2S(2.5 min-trap), ●: CS_2(2.5 min-trap), ◐: H_2S(5 min-trap), and ◑: CS_2(5 min-trap).
Conditions: Furnace temperature 900 °C.

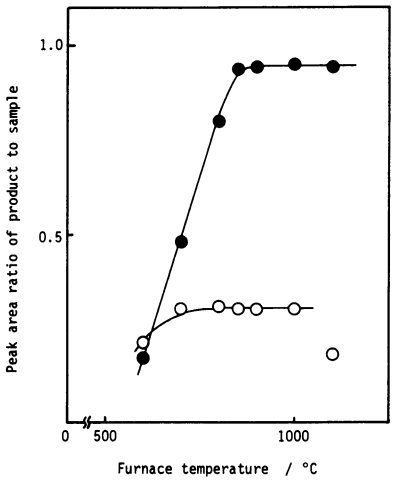

Fig. 5. Effect of furnace temperature on the amount of products.
○: H_2S and ●: CS_2. Conditions: Trap time 5 min.

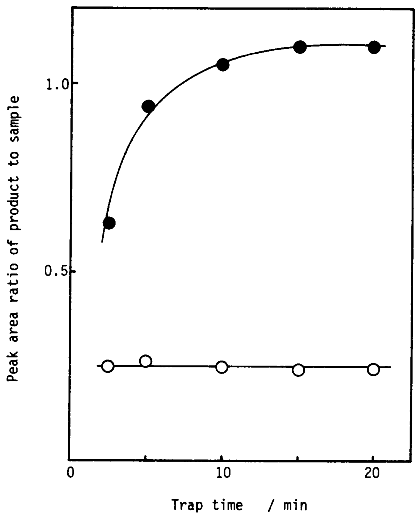

Fig. 6. Effect of trap time on the amount of products.
○: HS and ●: CS_2.

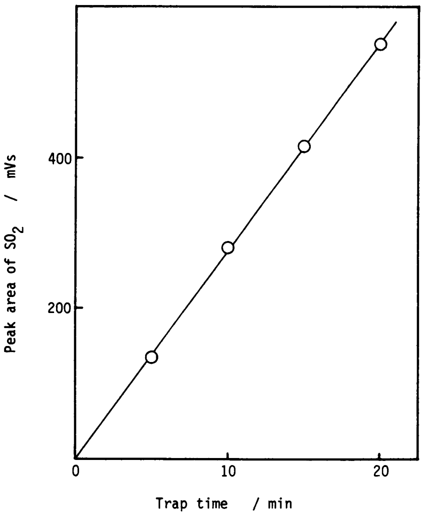

Fig. 7. Relationship between trap time and peak area of SO_2.

amount of sulfur dioxide (SO_2) was constantly produced from sulfur as its impurity, so the amount of SO_2 was measured in the range of 5—20 min of trap time by the use of the present system (Fig. 7). The amount of SO_2 is proportional to the trap time. It is generally better to minimize the analysis time and to simplify the data analysis in all qualitative identification. Therefore, the trap time for qualitative identification was chosen to 2.5 min after the elution of a target component from GC-I as its optimum condition by considering both the analysis time and the blank value of SO_2.

Reaction Products by Pyrolytic Sulfurization. The reaction products obtained by the pyrolytic sulfurization reaction under the above-mentioned conditions were investigated by subjecting several kinds of organic compounds to the GC-PSR-GC system. The reaction products were restricted to carbon dioxide (CO_2), COS, CS_2, H_2S, water (H_2O), SO_2, and HCN. Here each product was identified gaschromatographically by analyzing a authentic sample. The results showed that carbon in an organic compound is converted to CO_2, COS, CS_2, and HCN, hydrogen to H_2S, H_2O, and HCN, oxygen to CO_2, COS, SO_2, and H_2O, and nitrogen to HCN, respectively, by the pyrolytic sulfurization reaction under the present conditions. In order to separate and determine the seven kinds of the products by gas chromatography, their optimum conditions were searched and obtained, as described in experimental term. A typical chromatogram of the products is shown in Fig. 8. This was obtained by analyzing nitromethane as a target component, from which seven kinds of products were produced by the use of GC-PSR-GC. As can be seen from Fig. 8, seven kinds of products

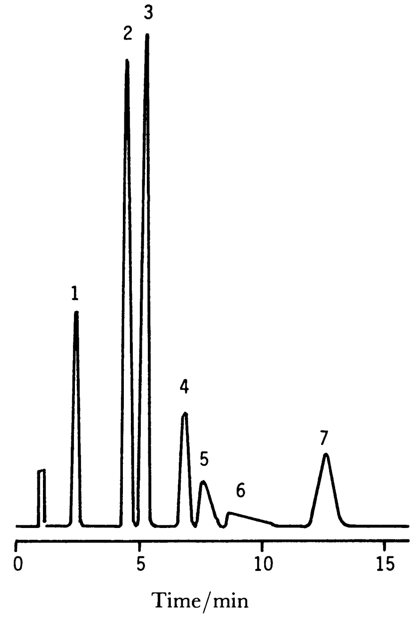

Fig. 8. Typical chromatogram of nitromethane.
1: CO_2, 2: H_2S, 3: COS, 4: SO_2, 5: HCN, 6: H_2O, and 7: CS_2.

Table 1. Analytical Results of Various Organic Compounds

Sample	Products[a]							Components	
	CO_2	H_2S	COS	SO_2	HCN	H_2O	CS_2	Theor.	Found
Toluene	−	+	−	−	−	−	+	CH	CH
Benzene	−	+	−	−	−	−	+	CH	CH
Hexane	−	+	−	−	−	−	+	CH	CH
Cyclohexene	−	+	−	−	−	−	+	CH	CH
Triethylamine	−	+	−	−	+	−	+	CHN	CHN
Ethylenediamine	−	+	−	−	+	−	+	CHN	CHN
Pyridine	−	+	−	−	+	−	+	CHN	CHN
Acrylonitrile	−	+	−	−	+	−	+	CHN	CHN
Methyl alcohol	+	+	+	−	−	−	+	CHO	CHO
Ethyl alcohol	−	+	+	−	−	−	+	CHO	CHO
Propyl alcohol	−	+	+	−	−	−	+	CHO	CHO
Butyl alcohol	−	+	+	−	−	−	+	CHO	CHO
Acetone	−	+	+	−	−	−	+	CHO	CHO
Ethyl methyl ketone	−	+	+	−	−	−	+	CHO	CHO
Isobutyl methyl ketone	−	+	+	−	−	−	+	CHO	CHO
Acetylacetone	−	+	+	−	−	−	+	CHO	CHO
Ethylene glycol monomethyl ether	−	+	+	−	−	−	+	CHO	CHO
Dibutyl ether	−	+	+	−	−	−	+	CHO	CHO
Methyl acetoacetate	+	+	+	−	−	−	+	CHO	CHO
Methyl acrylate	+	+	+	−	−	−	+	CHO	CHO
Acetic acid	+	+	+	−	−	−	+	CHO	CHO
Propionic acid	+	+	+	−	−	−	+	CHO	CHO
Nitromethane	+	+	+	+	+	+	+	CHON	CHON
Nitroethane	+	+	+	+	+	−	+	CHON	CHON
N, *N*-Dimethylformamide	−	+	+	−	+	−	+	CHON	CHON
Morpholine	−	+	+	−	+	−	+	CHON	CHON

a) +, −: Shows the production or non-production of the product.

can be successfully separated one from another and can be eluted within 15 min.

Qualitative Indentification of C, H, O, and N in a Standard Sample. Many kinds of organic compounds were analyzed by GC-PSR-GC by the use of 0.4 μl of sample; the products from the sample are shown in Table 1. With regard to all samples, carbon in a sample was mainly converted to CS_2 and COS, where CS_2 became a main product in a carbon-rich compound and COS did in an oxygen-rich compound, hydrogen to H_2S, oxygen to COS, and nitrogen to HCN. Therefore, the component elements: C, H, O, and N in an organic compound could be easily identified by observing four kinds of products: CS_2, COS, H_2S, and HCN; all the samples are shown in Table 1. The component elements in the sample can be qualitatively identified without any exceptions.

Detection Limit of GC-PSR-GC. The detection limit of GC-PSR-GC was examined under the present conditions by the use of ethanol and acrylonitrile as standard samples. No products except SO_2 were observed by the blank test under the present conditions, and a small amount of COS produced by the reaction between carbon in a target component and SO_2 as an impurity of sulfur was observed when the component containing no oxygen was analyzed. Therefore, the detection limit of the present method for the products except COS was defined as the signal to noise ratio equal to two on a gas chromatogram, while that for COS was also defined as the signal to blank ratio equal to two. As a result of the investigation on the basis of above definition, the detection limit of GC-PSR-GC was a few pmol.

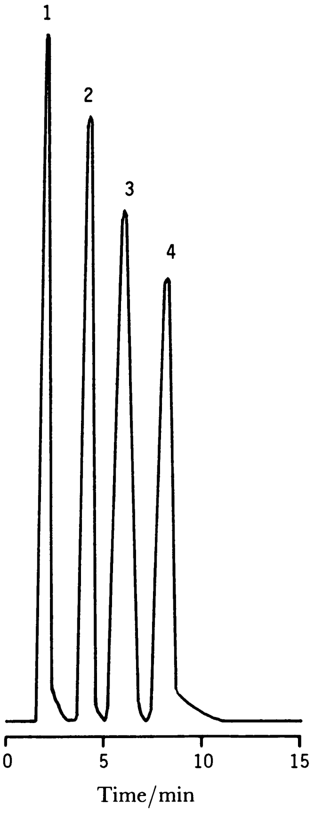

Fig. 9. Chromatogram of mixed sample by GC-I.
1: Methyl alcohol, 2: cyclohexene, 3: pyridine, and 4: morpholine.
GC conditions: Column stainless steel (3 mm i.d., 4 mm o.d., and 1 m long), column packings 5%-Silicone GE SE-30 on Chromosorb W (60—80 mesh), column temperature 60 °C, flow rate 11 cm³/min, and carrier gas He.

Identification of C, H, O, and N in a Component Separated from a Mixed Sample by Gas Chromatography. The mixed sample was artificially prepared by mixing four kinds of compounds: cyclohexene consisting of C and H, methanol consisting of C, H, and O, pyridine consisting of C, H, and N, and morpholine consisting of C, H, O, and N. This sample was subjected to GC-PSR-GC in the following manner. One μl of the sample was injected to GC-I(chromatogram of this sample is shown in Fig. 9) and the target peak of a sample was introduced to the pyrolytic sulfurization reactor by operating the four-way cock mounted with GC-I, followed by analysis by the present procedure. By repeating the above-mentioned procedure, four kinds of compounds in the mixed sample were analyzed. Each chromatogram is shown in Fig. 10. The component elements in each compound could be successfully and easily identified by the use of each chromatogram of the compound. These results indicate that all organic compounds which can be separated by gas chromatography can be subjected to GC-PSR-GC and can be qualitatively identified according to their component elements: C, H, O, and N. In other words, the present system can be expected to become a useful tool as a secondary

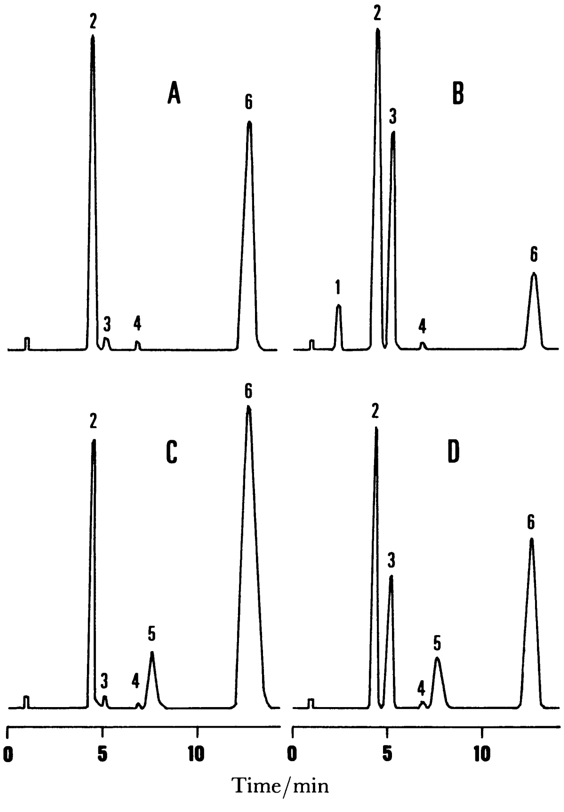

Fig. 10. Chromatograms of samples by GC-PSR-GC (A: cyclohexene, B: methyl alcohol, C: pyridine, and D: morpholine).
1: CO_2, 2: H_2S, 3: COS, 4: SO_2, 5: HCN, and 6: CS_2.

detector for gas chromatography.

Pyrolytic Sulfurization Reaction under the Present Conditions. Pyrolytic sulfurization reaction under the present conditions is discussed here on the basis of the results obtained in this study. Figure 4 indicates that the amount of CS_2 produced is influenced by the trap time, though that of H_2S is not, for each sulfur temperature. Figure 6 also indicates that the amount of CS_2 becomes constant by trapping it for over 15 min, while that of H_2S becomes constant within 2.5 min. These results can be explained by presuming the mechanism of pyrolytic sulfurization under the present conditions as follows: A target component is immediately decomposed in the furnace to gaseous compounds and carbon deposit. Then the gaseous compounds react with sulfur vapor during the passage through the reaction tube and the carbon deposit reacts with sulfur vapor at the position of the thermal decomposition until it is completely converted to CS_2. Therefore, the times necessary for the production of H_2S and CS_2 may be different. This was also experimentally proved by the use of other kinds of compounds.

Comparison of GC-PSR-GC with PSGC with Regard to Pyrolytic Sulfurization. Pyrolytic sulfurization gas chromatography(PSGC)[6-19] has been previously investigated and successfully established by the authors as a new elemental analysis method by which the atomic ratio between C, H, O, and N in an organic compound can be simultaneously determined. This method has been successfully applied to various organic compounds, such as an usual organic compound, a metal organic chelate, a polymer, and an organic halogen compound. In PSGC, a sample is made to react with sulfur in a sealed quartz tube for 1 min at 1500 °C or for 30 min at 950 °C. Therefore, a pyrolytic sulfurization reaction occurs at high pressure. On the contrary, pyrolytic sulfurization reaction by GC-PSR-GC occurs at atmospheric pressure, as described in this study. The reaction products obtained by GC-PSR-GC are the same as those obtained by PSGC, except for HCN. Nitrogen in a sample is converted to molecular nitrogen in PSGC. This suggests that the reaction conditions of PSGC are severer than those of GC-PSR-GC. The fact that pyrolytic sulfurization reaction by GC-PSR-GC is completed by reacting a sample with sulfur for 15 min at 900 °C, though the reaction by PSGC is done for 30 min at 950 °C may be explained as follows: Pyrolytic sulfurization reaction by PSGC may take a longer time to convert carbon in a sample to CS_2 at the end of the reaction. This suggests that a trace amount of carbon must react with a trace amount of sulfur at the end of the reaction since a stoichiometric amount of sulfur is present in the sealed tube, unlike the case of GC-PSR-GC.

On the basis of the above-mentioned investigation, a method for the qualitative identification of the component elements, C, H, O, and N, in an organic compound was newly established. This method, called GC-PSR-GC, is characterized by the following: 1) The component elements: C, H, O, and N, in an organic compound can be qualitatively identified, 2) data analysis is very simple, 3) this method is more simple and economical than earlier ones, and 4) this method is also useful as a secondary detector of gas chromatography. This method will contribute to progress in organic chemistry.

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