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A New Gas Sampler for Pyrolytic Sulfurization Gas Chromatography

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Synopsis. A new gas sampler was designed and constructed by the use of a commercially available pyrolytic apparatus. This sampler made easier heating and crushing an ampoule, and introducing a liberated gas into a gas chromatograph than those by the conventional gas sampler.

One of the most important operations in the pyrolytic sulfurization gas chromatography[1–4] was to introduce a liberated gas into a gas chromatograph. Therefore, a new gas sampler was constructed by combining a crushing device as shown in Fig. 1 with a Shimadzu PYR-1A pyrolyzer. The sampler thus constructed has advantages in heating and crushing an ampoule and introducing the liberated gas into a gas chromatograph compared with the conventional gas sampler. The elemental analysis of polymer and carboxylic acid samples was tried by the pyrolytic sulfurization gas chromatography with the new gas sampler. The results obtained were almost satisfactory.

Experimental

Apparatus. The axial compression load method was adopted to crush an ampoule containing a sample. Figure 1 shows the crushing device of the new gas sampler. The crushing device was made of a stainless steel tube of 170 mm in length, 8 mm in outside diameter and 6 mm in inside diameter, and the device had a junction at about 45 mm from the one end. By the use of this junction, crushed pieces was able to remove easily, and the inner part of the crushing device was easily cleaned. An ampoule containing a sample was placed at position C, and crushed by pushing plunger D to the direction of the torsion. The gas sampler was heated by electric furnace F and the carrier gas was passed through A to B. The crushing device was combined with a Shimadzu PYR-1A pyrolyzer, and gas chromatograms were taken on a Shimadzu GC-4B gas chromatograph.

Reagents. Sulfur used as reagent was obtained by purifying[5] commercially available sulfur (chemical pure). Homopolymers, copolymers and terpolymers used as samples were commercially available products. Carboxylic acids and other organic compounds used as samples were of JIS special grade.

Procedure. The liberated gas was introduced into a gas chromatograph by either of the following two methods by operating a carrier gas stopcock of the pyrolytic apparatus: (a) An ampoule containing a sample was crushed while a carrier gas was passing through the crushing device. (b) An ampoule containing a sample was crushed while the carrier gas was stopped in the crushing device, and the liberated gas was introduced into the gas chromatograph with the carrier gas. In both cases, the introduced gas was analyzed under the following conditions: For polymer samples, a 2 m Silica-gel (60—80 mesh) column was used at the flow rate of 50 ml min^{-1} He carrier, and for carboxylic acid samples, a 0.25 m Chromosorb 104 (80—100 mesh) column connected with a 1.75 m Porapak Q (80—100 mesh) column in series was used at the flow rate of 30 ml min^{-1}. All the chromatograms were obtained at the programmed temperature of 20 °C min^{-1} over 80—180 °C.

Results and Discussion

Both ends of an ampoule containing a sample were conical and sharp. Figure 2 shows the crushing direction of an ampoule containing a sample. It was proved from the results of compression test (n=3) by means of a Toyo Baldwin UTM-5000-E universal testing machine of Fukui industrial laboratory that the axial compression load (A) (within 10 kg) necessary for crushing an ampoule containing a sample was smaller than the lateral compression load (B) (about 40 kg).

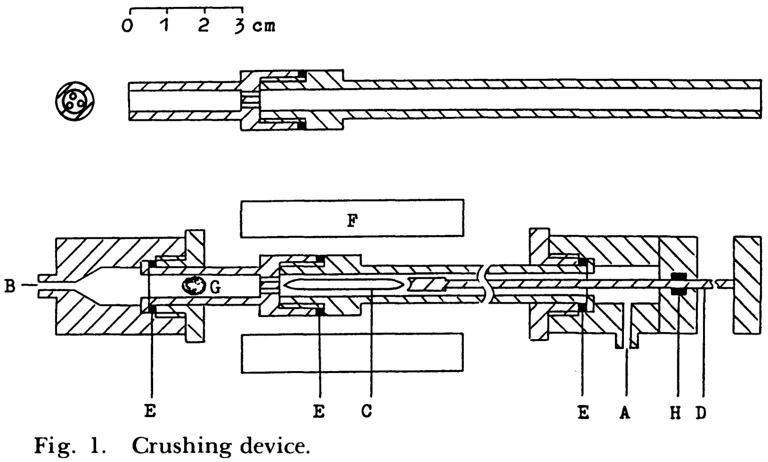

Fig. 1. Crushing device.
A: Carrier gas inlet, B: carrier gas outlet, C: ampoule containing a sample, D: plunger for crushing an ampoule, E: seals, F: electric furnace, G: filter, and H: silicone rubber gasket.

Table 1. Analytical results of polymers

Sample	C/wt%		H/wt%		O/wt%		N/wt%	
	CH Anal.[a]	PSGC	CH Anal.[a]	PSGC	CH Anal.[b]	PSGC	CH Anal.[a]	PSGC
Nylon	63.68	63.41	9.80	9.53	14.14	14.33	12.73	11.72
Polyethylene glycol	53.92	53.79	9.39	9.67	36.69	36.54		
Poly(vinyl alcohol)	52.86	52.56	8.92	9.13	38.22	38.31		
Methyl methacrylate-styrene copolymer	76.05	76.08	8.15	8.48	15.80	15.44		
Acrylonitrile-stylene copolymer	85.66	85.30	7.20	7.26			7.14	7.44
Methyl methacrylate-acrylonitrile-styrene copolymer	81.19	81.38	7.76	7.98	6.26	5.99	4.79	4.65
Acrylonitrile-butadiene-stylene copolymer	85.26	85.68	8.11	7.90			6.63	6.42

a) The sample compositions analyzed at the Elemental Analysis Center of the Pharmaceutical Department of Kyoto University. b) Obtained by subtracting the sum of the C, H, and N values from the total amount of a sample. Column: Silica gel 2 mX4ϕ SUS; Column temp: 80°C→180°C(20°C/min); Carrier gas: He 50 ml min^{-1}.

Table 2. Analytical results of carboxylic acids

Sample	C/wt%			H/wt%			O/wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
Heptadecanoic acid	75.50	75.35	0.15	12.67	12.94	0.27	11.83	11.71	0.21
Benzoic acid	68.86	68.68	0.16	5.00	5.05	0.05	26.16	26.27	0.11
Tartaric acid	32.01	32.06	0.05	4.03	4.02	0.01	63.96	63.92	0.04
Mandelic acid	63.15	63.36	0.21	5.30	5.38	0.08	31.55	31.26	0.29
Malic acid	35.83	35.92	0.09	4.51	4.55	0.04	59.66	59.53	0.13
p-Hydroxybenzoic acid	60.87	60.59	0.28	4.38	4.57	0.19	34.75	34.84	0.09
Gallic acid	44.69	45.01	0.32	4.29	4.21	0.08	51.02	50.78	0.24

Column: Chromosrb 104 0.25 mX4ϕ SUS and Porapak Q 1.75 mX4ϕ SUS; Column temp: 80°C→180°C(20°C/min); Carrier gas: He 30 ml min^{-1}.

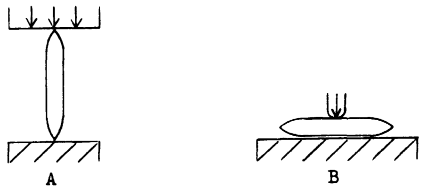

Fig. 2. Crushing direction of an ampoule containing a sample.
A: Axial compression, and B: lateral compression.

Therefore, the crushing method by means of the axial compression load was adopted in the following experiment. This crushing method was easily carried out by pushing the plunger in the crushing device shown in Fig. 1. The gas in an ampoule is easily liberated because the ampoule is dashed to pieces. When the liberated gas was introduced into the gas chromatograph, both the methods, (a) and (b), mentioned above gave the same gas chromatogram. The (a) method was not always applicable on account of the imperfect crushing of an ampoule, while the (b) method was always possible after confirmation of the complete crushing of an ampoule. Tables 1 and 2 show the results of elemental analyses of polymers by the (a) method, and carboxylic acids by the (b) method, respectively. Both organic halogen and organometallic compounds were also analyzed and reasonable results were obtained. This new gas sampler has the following features: (1) Connecting the gas sampler with a pyrolyzer is easier than attaching the conventional gas sampler to a gas chromatograph directly. (2) Heating and crushing an ampoule are easier than those in the conventional gas sampler. (3) The load necessary for crushing an ampoule is less than that for the conventional gas sampler. (4) Analytical operation can be continuously performed by using a carrier gas stopcock of a pyrolytic apparatus.

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