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## Note

### Porous sulphonic acid resins as subtractor for olefins in gas chromatography

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Subtractor columns in gas chromatography (GC) are useful in the analysis of functional groups and the removal of interfering peaks. Subtractor columns containing sulphuric acid have been applied to the analysis of hydrocarbons<sup>1-4</sup> and the constituents in air<sup>5</sup> based on their ability to remove olefins. Hoff and Feit<sup>6</sup> investigated the reactivity of syringe reactor containing sulphuric acid and different gaseous components, and the reactor is applied to the functional group analysis.

We have found that a column packed with a porous ion-exchange resin containing sulphonic acid as the functional group (SO<sub>3</sub>H resin) was similar to a sulphuric acid column with respect to specific reactivity. This paper describes the reactivity of the SO<sub>3</sub>H resin column and the removal of olefins from hydrocarbons in GC. Although SO<sub>3</sub>H resin is well known as a cation exchanger, it has also been investigated as a column packing. Porous SO<sub>3</sub>H resin and its metal forms have been used as a column packing in the separation of hydrocarbons<sup>7,8</sup>, and SO<sub>3</sub>H resin with reduced active nickel metal has also been used in the GC separation of carbon monoxide and carbon dioxide<sup>9</sup>. However, only the nickel and copper forms of SO<sub>3</sub>H resin are applied in subtractors for amines in GC<sup>10</sup>. Generally, with a sulphuric acid subtractor column, steps must be taken to preserve the column<sup>1,2</sup> because of its strongly hygroscopic nature. It is expected that the SO<sub>3</sub>H resin column proposed here will be easier to handle than a sulphuric acid column.

#### EXPERIMENTAL

##### *Apparatus and reagents*

A Shimadzu GC-4APF gas chromatograph equipped with dual hydrogen flame-ionization detectors was used for the evaluation of the subtractors. The surface properties and thermal analysis of the polymer beads were studied with the apparatus reported previously<sup>11</sup>. A standard gas mixture (ethane 1.32%, ethylene 1.19%, propane 1.01%, propylene 1.65%, isobutane 1.00% and *n*-butane 0.967% in nitrogen), ethylene (99.5%), propylene (99.5%) and 1-butene (8% in nitrogen) were obtained

from Gasukuro Kogyo (Japan). Other reagents were of commercial reagent grade and used without further purification.

#### Preparation of $SO_3H$ resin

A 10-g portion of porous styrene-divinylbenzene (DVB) copolymer beads (7.5, 15, 30% DVB) or gel beads (15% DVB) was suspended in 75 ml of concentrated sulphuric acid containing 0.1 g of silver sulphate as the catalyst. The mixture was stirred for 6 h at 90°C with the porous beads and 6 h at 120°C with the gel beads. Then the reaction mixture was transferred into ice-water. The resulting resin was washed with water and recycled several times between the sodium and hydrogen forms with 1 *M* sodium hydroxide solution and hydrochloric acid. After washing with water, the resin was rinsed with methanol and dried at 50°C. The 60–80-mesh fraction was collected.

#### Gas chromatography

Unless otherwise stated, the columns used were 1.5 m × 4 mm I.D. glass columns consisting of a subtractive pre-column (10 cm) and an analytical column (1.4 m) packed with Unibeads 3S (60–80 mesh, Gasukuro Kogyo) for analysis of hydrocarbons, and 1.5% SE-30 on 60–80-mesh Chromosorb W AW DMCS for the analysis of other compounds. The columns were conditioned at 140°C for 3 h. Nitrogen was employed as the carrier gas at a flow-rate of 60 ml/min, and 0.5 ml of sample (concentration 10<sup>3</sup> ppm in nitrogen) was injected into the column. The percentage removal of the compounds was determined by comparing their peak areas in the presence and absence of the subtractive pre-column.

### RESULTS AND DISCUSSION

Sulphonated ion-exchange resins having different surface properties and capacities were investigated in order to evaluate their subtractive properties for olefins in GC. The physical properties of the resins used are summarized in Table I. The columns packed with porous type resins II, III and IV subtracted olefins from their chromatograms, but not alkanes, whereas, resin I (gel type) showed no marked af-

TABLE I  
CHARACTERIZATION OF  $SO_3H$  RESINS

Resin (DVB, %)	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)	Exchange capacity (mequiv./g)	Analysis: S (%) (mequiv./g)
I (15%)	0	0	0	4.00	13.95 (4.36)
II (7.5%)	27.0	0.047	7.0	4.05	12.93 (4.04)
III (15%)	42.5	0.075	7.1	3.90	13.58 (4.24)
IV (30%)	60.4	0.144	9.5	2.45	8.54 (2.67)

finity toward olefins under the same conditions. The porous structure of the resins seems to be an essential factor for the subtractive column packing in GC.

In order to characterize resins II, III and IV as column packings, the retention behaviour of *n*-hexane was tested. With increasing surface area of the resins, the retention times of *n*-hexane tends to increase and the peak is broadened. Resin III, which has a suitable surface area for subtraction of olefins, was used in subsequent experiments.

The percentage removal for various hydrocarbons with the subtractor column packed with resin III is shown in Table II. Of the olefins tested, only ethylene is not retained quantitatively on the column and its peak is broadened. The percentage removal of ethylene increases with increase in the column temperature. Ethylene also showed a low percentage removal using the subtractor column containing sulphuric acid<sup>1,3</sup>.

Previously we reported that the hydrosulphate form of a porous poly(vinylpyridine) bead column<sup>12</sup> does not subtract olefins. This suggests that free sulphuric acid is required for the subtraction of olefins, and sulphonic acid groups on the resin show a similar reactivity toward olefins.

For the mechanism of the subtractive reaction of olefins with the proposed resin, the following possibilities were considered: (1) addition of sulphonic acid group to olefin; (2) formation of a hydrogen bond between the double bond and the hydro-

TABLE II  
PERCENTAGE REMOVAL OF HYDROCARBONS BY RESIN III

Class	Compound	Column temperature (°C)	
		30	140
Alkanes	Ethane	17	—
	Propane	0	—
	<i>n</i> -Butane	0	—
	Isobutane	0	—
	<i>n</i> -Pentane	—	0
	<i>n</i> -Hexane	—	0
	<i>n</i> -Octane	—	0
	Cyclohexane	—	0
Olefins	Ethylene	38	79
	Propylene	100	98
	1-Butene	100	99
	1-Pentene	—	100
	2-Pentene	—	100
	1-Hexene	—	100
	2-Hexene	—	100
	1-Octene	—	100
	2-Octene	—	100
	Cyclohexene	—	100
Aromatic hydrocarbons	Benzene	—	4
	Toluene	—	48
	Ethylbenzene	—	38
	Styrene	—	100

TABLE III  
EFFECT OF CONDITIONING TEMPERATURE OF RESIN III

Conditioning time: 3 h.

Temperature (°C)	Removal of 1-pentene (%)*
30	16
80	84
120	99
140	100

\* The percentage removal was determined at the same temperature as conditioning.

gen atom on the sulphonic acid group; and (3) polymerization of olefins by a catalytic reaction. However, it is presumed that the reaction mode in the column may vary with the column temperature.

Small amounts of decomposition products amounting to less than 1% of olefin added were observed at a column temperature of above 80°C. However, normally these products cause no trouble and they were not subjected to a detailed study.

In order to check the column life, 0.5 ml of 1-pentene ( $10^4$  ppm in nitrogen) was injected repeatedly at 140°C, but no leakage of 1-pentene was observed with up to 50 injections.

The effect of the flow-rate of carrier gas on the removals of olefins was examined by using 1-pentene and 2-pentene at 80 and 120°C. No significant effect was observed at flow-rates between 30 and 120 ml/min.

The percentage removal varied with the temperature of column conditioning,

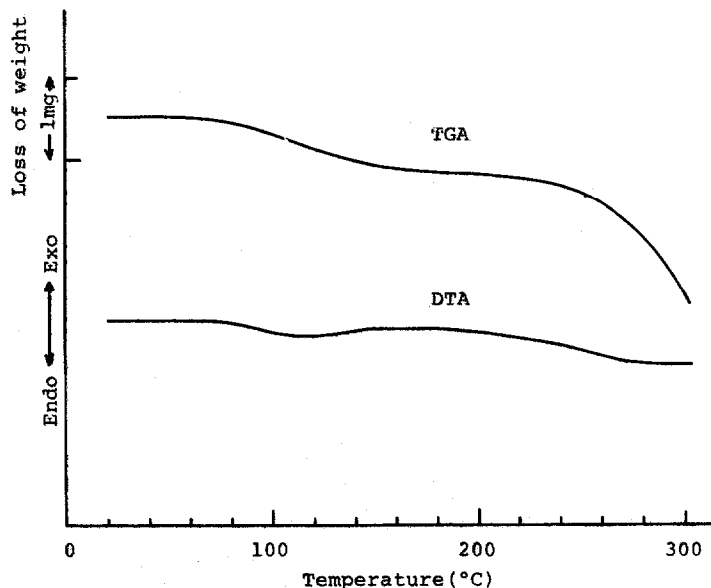


Fig. 1. TGA and DTA curves of resin III in a nitrogen atmosphere. Amount of sample for TGA: 10.95 mg.

TABLE IV

PERCENTAGE REMOVAL OF VARIOUS COMPOUNDS BY RESIN III AT A COLUMN TEMPERATURE OF 140°C

Type	Sample	Removal Type (%)	Sample	Removal (%)	
Alcohols	Methanol	100	Ketones	Acetone	100
	Ethanol	55		Methyl isobutyl ketone	100
	<i>n</i> -Propanol	92		Ethers	Diethyl ether
Alkyl halides	Chloroform	46	Tetrahydrofuran		100
	1,2-Dichloroethane	30	Sulphur compounds	Ethyl mercaptan	100
				Diethyl sulphide	100

and the results are shown in Table III. It is suspected that the sulphonated resins contain a fairly large amount of water, and the content of water may affect the reactivity. However, the column conditioned at 140°C for 3 h retained the olefins quantitatively at column temperatures of 30–140°C. During the conditioning, the resin must be activated with the dehydration, and the activation is necessary for the subtraction of olefins in this column.

The thermal stability of the resins was examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The four resins listed in Table I show similar thermal behaviour, and typical TGA and DTA curves for resin III are shown

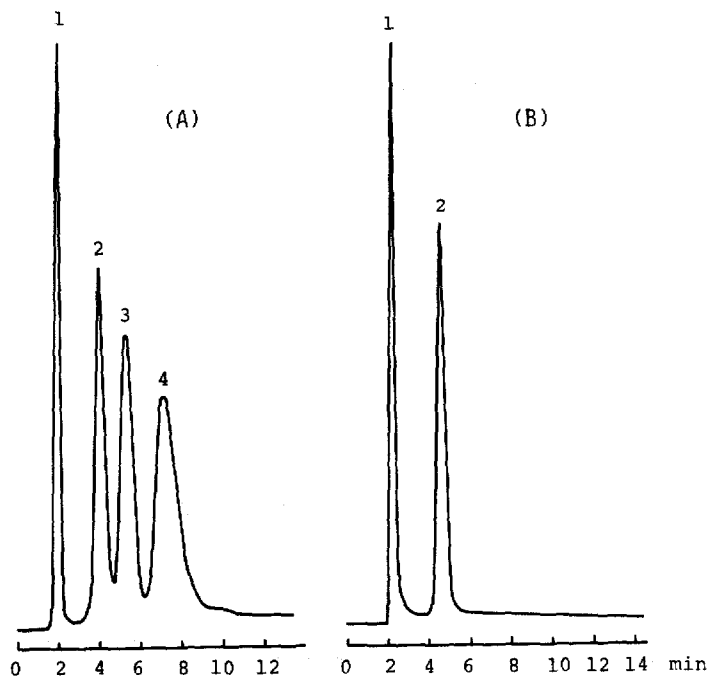


Fig. 2. Chromatograms for a mixture of *n*-pentane (1), *n*-hexane (2), 1-pentene (3) and 2-pentene (4). (A) Unibeads 3S (1.4 m); (B) resin III (10 cm) + Unibeads 3S (1.4 m). Sample size: 0.5 ml (the concentration of each hydrocarbon was 1000 ppm in nitrogen). Temperature: 80°C.

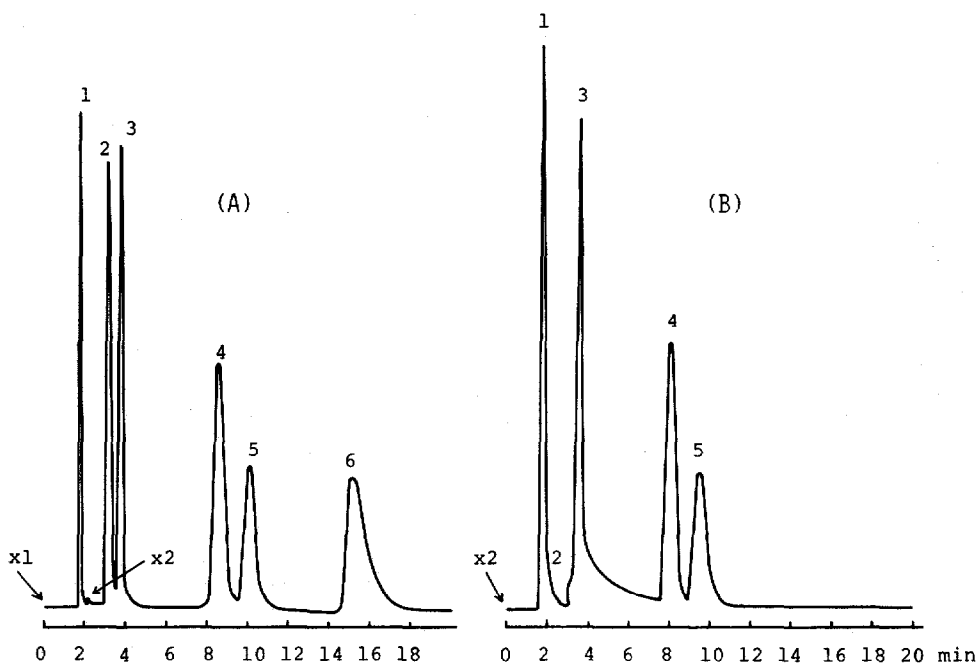


Fig. 3. Chromatograms of standard gas mixture. (A) Unibeads 3S (1.9 m); (B) resin III (10 cm) + Unibeads 3S (1.9 m). Peaks: (1) ethane; (2) ethylene; (3) propane; (4) isobutane; (5) *n*-butane; (6) propylene. Sample size: 50  $\mu$ l of the standard gas mixture. Temperature: 30°C. Carrier gas flow-rate: 30 ml/min.

in Fig. 1. A marked weight loss is observed in TGA between 55 and 180°C, and a small exothermic change in DTA is revealed between 70 and 150°C. The change in the thermograms up to 180°C may correspond to the loss of the water adsorbed on the resins. However, decomposition of the resins is unavoidable above 180°C, and we operated at maximal temperature of 140°C.

The removal of various compounds, other than hydrocarbons, is shown in Table IV. These data, except for ethanol, are similar to those for the sulphuric acid column<sup>2,5,6</sup>. The low value for ethanol may be attributable to the production of ethylene.

Figs. 2 and 3 show data for the separation of hydrocarbons with the proposed subtractor column. The subtractor retained completely the olefins except for ethylene, which was partly retained and overlapped with the peak of propane. In the chromatograms from the subtractor column, the peak height of ethane was halved and the peak was broad. The peaks of other alkanes were scarcely affected.

In conclusion, the proposed subtractor is useful for the removal of olefins from alkanes, and its advantages over sulphuric acid are that there is no bleeding of the corrosive acid, less interference to the free flow of the carrier gas and easier handling.

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