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Selective Removal of Carbonyl Compounds in Gas Chromatography by the Use of New Subtractor Column

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A subtractor column for aldehydes and ketones in gas chromatography was proposed. Crude acrylhydrazide, without troublesome purification, was used for the coating material. The column showed a stronger affinity for carbonyl compounds than the porous polymer containing hydrazide groups reported previously. Alcohols, hydrocarbons, ethers, and esters were not subtracted by this column. Concentration of the liquid phase and column temperature affected the subtraction of carbonyl compounds and the column life.

Keywords——acrylhydrazide; coating material; reaction gas chromatography; subtractor column; removal of carbonyl compounds

Selective removal of a limited number of peaks from gas chromatogram based on the formation of nonvolatile compounds with the packing material of a column is useful in gas chromatographic analysis. On the basis of this principle, we previously reported the use of a column packed with a porous polymer containing hydrazide groups (PPH) for the removal of aldehydes and ketones in gas chromatography.[2] Although this column has both characters, subtraction of carbonyl compounds and peak resolution of other compounds, synthesis of the porous polymer is rather tedious and time-consuming. The present paper describes the use of a crude acrylhydrazide as subtractor of the carbonyl compounds.

Experimental

Apparatus and Reagents——The gas chromatograph used was a Shimadzu GC-4APF equipped with dual hydrogen flame detectors. The mean molecular weight was measured with a vapor pressure osmometer model 302 (Mechro lab.) at 37° in EtOH. Kinematic viscosity was measured with Ostwald viscometers.

All the samples used, except aldehydes, were analytical grade reagents without further purification. Aldehydes were purified before use by distillation in N_2 atmosphere.

Preparation of Coating Material——Five ml of hydrazine hydrate was allowed to react with 5 ml of ethyl acrylate at room temperature, then the reaction mixture was evaporated at a reduced pressure (20 Torr) at 70—80°. The reaction product was dissolved in 10 ml H_2O, and the solution was evaporated under the above condition. This procedure was repeated 5 times to remove unreacted hydrazine hydrate and the product was dried at a reduced pressure (2 Torr) for 3 hr at 100°. The final product was a hygroscopic, viscous and colorless liquid. *Anal.* Calcd. for $C_3H_6N_2O$: C, 41.85; H, 7.02; N, 32.54. Found: C, 40.88; H, 7.30; N, 32.41. MS *m/e*: 86 ($C_3H_6N_2O^+$), 172 (86×2). IR $^{liq}_{max}$ cm^{-1}: 3260 (ν_{NH}), 1650 ($\nu_{C=O}$), 1540 (δ_{NH}). Mean molecular weight: 190. Kinematic viscosity: 1350 cs at 60°. The reactivity of this compound was determined in the following way. An appropriate amount of the sample (250—300 mg) was shaken with 5 ml of aqueous acetone solution (5%) for 24 hr at room temperature. The amount of reduced acetone was determined by gas chromatography (column: 5% dinonyl phthalate). Amount of reacted acetone: 6.3 meq/g (value calculated based on N% of the sample: 11.6 meq/g).

Gas Chromatography——The column (3 m × 4 mm i.d., glass column) was composed of 1 m subtractor precolumn and 2 m analytical column (5% dinonyl phthalate on 60/80 mesh Shimalite W). The precolumn was prepared from EtOH solution of the crude acrylhydrazide and 30/60 mesh Shimalite in the usual way. A typical gas chromatographic condition was as follows: column oven temperature, 80—110°; detector temperature, 180°; carrier gas, N_2 60 ml/min; sample size, 0.3 μl. Percentage of the compounds removed were determined by comparing their peak areas, both in the presence and absence of the precolumn.

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Results and Discussion

It is known that the reaction products of α,β-unsaturated carboxylic acid esters with hydrazine hydrate contain pyrazolidones.[3] Rondestvedt and Chang[4] also reported that acrylhydrazide obtained by the reaction of methyl acrylate with anhydrous hydrazine cyclizes and the product does not condense with acetone. The proposed coating material is presumed to be a mixture of 3-pyrazolidone, and a monomer and oligomer of acrylhydrazide.[3] However, it is clear from the experimental data that the crude product contains free hydrazide groups (6.3 meq/g). Consequently, in this study we used the crude acrylhydrazide for the coating material without troublesome purification.

The effect of column temperature and concentration of liquid phase on the percentages of some compounds removed is summarized in Table I. When the concentrations of liquid phase are 30% or above, all the aldehydes and ketones except branched-chain methyl ketones were quantitatively subtracted. The percentages of methyl isopropyl ketone and isobutyl ketone removed decreased with increase of the column temperature. Similar behavior has been observed in PPH.[2] No difference in the subtraction of the carbonyl compounds was observed between 30 and 50% of the liquid phase. γ-Butyrolactone, which was partially subtracted by PPH, was quantitatively subtracted by the proposed column. This fact shows that the reactivity of acrylhydrazide for the carbonyl groups is higher than that of the hydrazide group on the polymer cross-linked with divinylbenzene. 1,2-Dichloroethane and chloroform were also partially subtracted by this column, while ethers, hydrocarbons, esters, and alcohols were not subtracted on the column. However, the peaks of alcohols were broadened and delayed, compared with those in the reference column (5% dinonyl phthalate).

Table I. Removal of Compounds at Different Temperatures

Compounds	Concentration of liquid phase (%)	Removal (%) Column temp. 80°	100°	110°
Aldehydes (nC_3-nC_6)	10	100	100	100
	30	100	100	100
	50	100	100	100
Methyl ketones (nC_1-nC_4)	10	100	100	100
	30	100	100	100
	50	100	100	100
Methyl isopropyl ketone	10	35	33	12
	30	100	98	91
	50	100	98	90
Methyl isobutyl ketone	10	44	44	41
	30	100	97	92
	50	100	97	93
Cyclohexanone	30	100	100	100
γ-Butyrolactone	30	100	100	100
Chloroform	30	22	26	28
1,2-Dichloroethane	30	8	13	14

In order to determine the column life, methyl isopropyl ketone was injected successively 100 times. The deterioration of the column was slight at the column temperature of 80°, but at 100° it was not negligible. The percentage removal fell to 92% at 100° after 100 times

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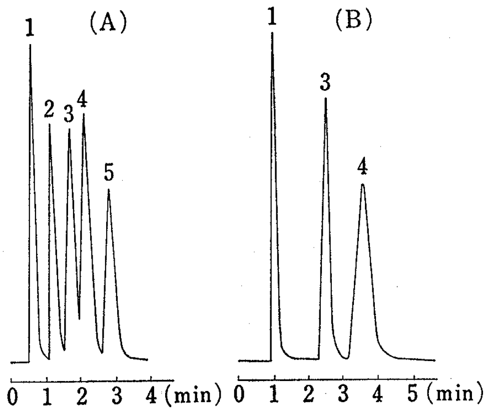

Fig. 1. Gas Chromatograms of a Mixture Illustrating Effect of Proposed Column

(A) 5% dinonyl phthalate (2 m), (B) 30% crude acrylhydrazide column (1 m) +5% dinonyl phthalate column (2 m), column temp., 80°. 1, diisopropyl ether; 2, methyl isopropyl ketone; 3, octane; 4, toluene; 5, methyl butyl ketone

of injection. This fact would show that this column had a sufficient capacity at 80°. In addition, the column was applicable to the aqueous solution such as 1% acetone solution.

As the subtractor column cannot resolve most of the compounds, use of another analytical column is necessary for sufficient resolution of the peaks. An example of simultaneous use of the crude acrylhydrazide and 5% dinonyl phthalate column is shown in Fig. 1. This column subtracts the ketones presented in the sample, and these ketones are recognized by the absence of their peaks when the chromatogram is compared with that obtained by the dinonyl phthalate column.

The important advantages of this column, compared with those of PPH, are that it is more reactive, easy to prepare, and inexpensive. This column would also be useful for the removal of the peak of a carbonyl compound used as a solvent, such as acetone, from the gas chromatogram in which the solvent peak often covers up those of other sample constituents.

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