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Use of Porous Polymer Containing Hydrazide Groups for Selective Removal of Carbonyl Compounds in Gas Chromatography

Atsushi Sugii, Kumiko Harada, and Naotake Ogawa

Faculty of Pharmaceutical Sciences, Kumamoto University[1]

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An evaluation of a porous polymer containing hydrazide groups as a subtractor for aldehydes and ketones in gas chromatography was described. Reactive species were subtracted in the gas phase due to the formation of hydrazone derivatives on the polymer and could be identified by their absence in the chromatograms. The proposed stationary phase had selectivity for aldehydes and ketones, while alcohols, esters, ethers, halides, hydrocarbons and water showed no effect.

Keywords——porous hydrazide polymer; gas chromatography; removal of carbonyl compounds; thermal stability; azines

Method of identification of functional groups by reaction gas chromatography has been noted for a simple technique which is applicable to the analysis of complex mixtures of organic compounds. There have been some investigations in which applications of the method to the removal of carbonyl compounds in gas chromatographic system are described: packed columns containing *o*-dianisidine,[2–4] benzidine,[2–4] hydroxylamine,[5] semicarbazide,[4] and bisulfite[2] are studied. Precolumn reactors packed with metal hydrides[6] are also applied for the same purpose. In all cases combination of short subtractor column and analytical column is used, and the main disadvantage is short life of subtractor columns.

On the other hand, Ashes and Haken[7] have reported an application of gas chromatography (GC) in which some stationary phases coated with aminoalkyl polysiloxanes subtract carbonyl compounds. They describe that these compounds can be operated at higher temperature and have greater specificity.

Since Hollis[8] has used porous polymers as the column packing for GC, their application has been extended by a number of investigators. However, the investigation of porous polymers having functional groups which react with only limited compounds has not been studied in GC. In the present study, a porous polymer containing hydrazide groups has been synthesized and applied to the column packing in GC. The proposed polymer permits the subtraction of aldehydes and ketones in the gas phase without interference from many other substances including water.

Experimental

Preparation of Polymers——The method of Emoto, *et al.*[9] was modified for the preparation of porous polymers used in this investigation. The synthetic pathway was shown in Chart 1.

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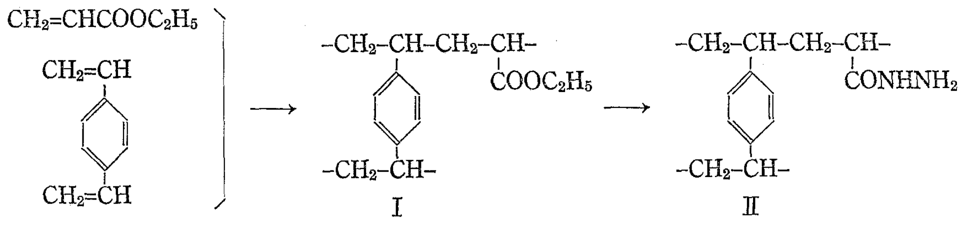

Chart 1

Porous Type Ethyl Acrylate-Divinylbenzene Polymer(I): Ethyl acrylate (105 g) and 50% divinylbenzene (45 g) were copolymerized in the presence of isooctane (150 ml), 0.4% polyvinyl alcohol aqueous solution containing 37.5 g of NaCl (750 ml) and benzoyl peroxide (2.25 g) by the suspension method. IR (KBr) cm^{-1}: 1735 (C=O).

Porous Type Hydrazide Polymer(II): Porous (I) (30 g) was treated with 120 g of anhydrous hydrazine at 120° for 12 hr. Thus obtained polymer was washed with successive 2 liter of water and 500 ml of MeOH and dried *in vacuo*. *Anal.* Found: N, 10.3. IR (KBr) cm^{-1}: 3300 (NH), 1735 (C=O). 1610—1665. Adsorbed amount of acetone[9]: 2.6 mmol/g. Cationic capacity: 0.4 meq/g.

Gel Type Hydrazide Polymer: Gel type ethyl acrylate-divinyl-benzene polymer (15% divinylbenzene) was allowed to react with anhydrous hydrazine under the same condition as porous polymer. *Anal.* Found: N, 14.4. IR (KBr) cm^{-1}: 3300 (NH), 1735 (C=O), 1610—1665. Adsorbed amount of acetone: 3.9 mmol/g. Cationic capacity: 0.6 meq/g.

Gas Chromatography——A Shimadzu GC-4APF gas chromatograph equipped with dual hydrogen flame detectors was used. The chromatographic columns used were glass, 1 m×4 mm i.d., packed with 60/100 mesh polymers. The flow rate of the nitrogen carrier gas was 60 ml unless otherwise noted. The average sample size was 0.3 μl per component. All the samples except for aldehydes were commercial high purity chemicals, and used without further purification. The aldehydes were purified by distillation under a nitrogen stream before use.

Thermal Analysis——The measurements of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were made with Shimadzu thermoflex apparatuses, DT-20B and TG-20, in a dynamic nitrogen atmosphere and at a heating rate of 10°/min.

Gas Chromatography–Mass Spectrometry (GC-MS)——Combination GC–MS was performed on JEOL–JMS 01SG instrument equipped with 1 m×3 mm i.d. glass column packed with porous polymer(II). The mass spectrometer was operated at an electron energy 27 eV and the gas chromatographic column temperature of 150°.

Results and Discussion

Thermal stability of the porous polymers was studied by DTA and TGA. DTA and TGA curves of porous II measured in a nitrogen stream were shown in Fig. 1. Endothermic change (20—90°) observed in DTA curve of the II is dependent on the adsorbed water and small peak at 90° is presumed to be glassy transition point which has been shown in the other polymers.[10] At the temperature above 160°, endothermic degradation of II takes place, while I shows no remarkable change up to 220° except for the glassy transition at 90°. Accordingly, conditioning of the column packed with I and II was carried out at 155°.

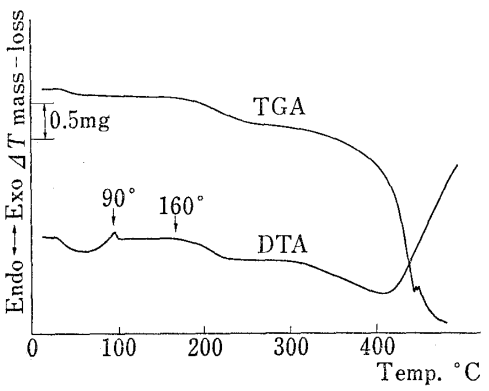

Fig. 1. TGA and DTA Curves of Porous Hydrazide Polymer

amount of sample for TGA; 8.0 mg

Per cent removal of the compounds by porous polymer (II) was listed in Table I. Although aldehydes and most ketones tested were essentially removed, branched chain ketones, methyl isopropyl ketone and methyl isobutyl ketone, only partially removed. It is considered that

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[10] For example: *a*) K.J. Bombaugh, C.E. Cook, and B.H. Clampitt, *Anal. Chem.*, 35, 1834 (1963); *b*) T.J. Dudek and J.J. Lohr, *J. Appl. Polymer Sci.*, 9, 3795 (1965).

Table I. Removal of Various Compounds at Different Temperature by Porous Hydrazide Polymer

Compounds	Removal (%)		
	100°	130°	150°
Propylaldehyde	100	100	100
Butyraldehyde	100	100	100
Isobutyraldehyde	100	100	100
Valeraldehyde	100	100	100
Caproaldehyde	100	100	100
Benzaldehyde	100	100	100
Acetone	100	100	100
Methyl ethyl ketone	100	100	100
Methyl propyl ketone	100	100	100
Methyl isopropyl ketone	98	96	86
Methyl butyl ketone	100	100	100
Methyl isobutyl ketone	98	98	85
Cyclohexanone	100	100	100
1,2-Butylene oxide	42	36	16
γ-Butyrolactone	—	—	29

partial removal of the ketones is due to the steric hindrance. This is the behavior being common to the other substractors[3,4,7] that have been reported. On the other hand, epoxide and lactone also reacted with the hydrazide groups, but the percentage removal is lower than that of aldehydes and ketones. It is possible to enhance the percentage removal by decreasing of flow rate of carrier gas or lower operating temperature. The effect of the flow rate on the removal of methyl isopropyl ketone is shown in Table II.

In order to investigate the effect of water in the gas chromatographic system using the proposed column, removal of acetone in the aqueous solution was carried out. Even in the

Table II. Effect of Flow rate of Carrier Gas on Removal of Methyl Isopropyl Ketone

Carrier gas flow rate (ml/min)	Removal (%)
30	100
60	96
90	94

column temperature: 130°

Table III. Compounds not Removed by Porous Hydrazide Polymer

1. Alcohols
   - Methyl
   - Ethyl
   - Propyl
   - Isopropyl
   - Butyl
   - Isobutyl
   - *sec*-Butyl
   - *tert*-Butyl
   - Pentyl
   - Hexyl
2. Esters
   - Methyl acetate
   - Ethyl acetate
3. Hydrocarbons
   - Hexane
   - Heptane
   - Octane
   - Nonane
   - Decane
   - Dodecane
   - Tetradecane
   - Hexadecane
   - 1-Octene
   - 1-Decene
   - Cyclohexane
   - Benzene
   - Toluene
4. Halides
   - Chloroform
   - Carbon tetrachloride
   - Dichloromethane
   - 1,2-Dichloroethane
   - 1,1,2,2-Tetrachloroethane
5. Ethers
   - Dimethyl ether
   - Diethyl ether
   - Tetrahydrofurane
   - 1,4-Dioxane

presence of 99% of water, no effect was observed on the removal of acetone. Moreover, the water did not adversely affected the performance of the chromatographic system as steady baseline was maintained even at high attenuation settings. This suggests that direct injection of the aqueous sample solution can be adopted in the GC. Many other compounds, except for the compounds listed in Table I, were unaffected. The compounds tested were shown in Table III.

Although II shows high selectivity for aldehydes and ketones, one of the disadvantages is the formation of by-product, which appears usually as small broad hump on the base line with retention times longer than the parent carbonyl compounds. The by-product peak appeared in the subtraction of acetone was analyzed by GC-MS. It was identified as ketazine which had molecular ion peak at *m/e* 112 corresponding to $C_6H_{12}N_2$. Cronin[4] has reported the formation of the azines by semicarbazide precolumn. It is supposed that the similar reaction occurs in the case of polymeric hydrazide groups. Fortunately, it is possible to reduce the formation of azines to insignificant levels by maintaining the column at a moderately low temperature and isothermal conditions these compounds are often barely detectable.

Repeated use of II did not show the rapid deterioration that has been reported with other subtractor columns. The column used in this work was subjected to over 200 times injections of carbonyl compounds (0.3 μl/one injection) without deterioration.

Gel type hydrazide polymer was also examined for the subtractor of carbonyl compounds in GC as well as the porous polymer. In spite of its higher capacity the gel type hydrazide polymer showed lower removal of carbonyl compounds than the corresponding porous polymer: percentage removal of acetone at 100° was only 41%. This fact can be explained on the basis of porosity and large surface area of porous polymer.

Porous I and II have also an ability to separate various highly polar compounds as well as the conventional porous polymers such as Porapak T and Q. Accordingly, porous II can be used as the column packing having the both ability of subtraction and separation. However, the separation efficiency is not satisfactorily high: values for height equivalent to a theoretical plate of I and II are 5.7 mm and 30 mm for MeOH, respectively. In order to improve the separation efficiency, we are now under investigation on the modification of polymers.