POROUS HYDROCHLORIDE AND HYDROSULPHATE FORMS OF POLY-(VINYLPYRIDINE) BEADS AS SUBTRACTORS FOR AMINES AND ALCOHOLS IN REACTION GAS CHROMATOGRAPHY

ATSUSHI SUGII* and KUMIKO HARADA

Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi Kumamoto City, Kumamoto 862 (Japan)

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SUMMARY

The differential reactivity of a new subtractor column packed with acid forms of porous poly(4- or 2-vinylpyridine) toward amines and alcohols in gas chromatography has been studied. Primary and secondary amines were quantitatively subtracted by formation of stable salts on the column, but tertiary amines were not subtracted quantitatively. The hydrosulphate form of the polymer could subtract primary and secondary alcohols, but not *tert.*-butanol, which was dehydrated to the corresponding olefin. The hydrochloride form of the polymer had no affinity for the alcohols, except *tert.*-butanol, which was partially dehydrated. The application of the proposed subtractor columns was demonstrated by using a synthetic sample.

INTRODUCTION

Porous polymer beads, with a large surface area and a suitable porosity, have been widely utilized as column packings in gas chromatography (GC). When a porous polymer which has specific functional groups reactive only to particular compounds is used as a column packing, it is effective in functional groups analysis because the column retains only particular compounds in GC. It would be also useful to have a subtractor column with sufficient capacity and selectivity to eliminate the solvent peak from a gas chromatogram without affecting any of the sample peaks. However, there are few reports on the application of porous polymers as the subtractor in GC. Polymer beads having a hydrazide group[1] and nickel and copper forms of sulphonated Amberlite XAD-2 resin[2] have been applied for the subtraction of carbonyl compounds and amines, respectively.

We have previously reported the usefulness of porous poly(vinylpyridine) beads as a column packing for the GC separation of amines[3]. It was found that hydrochloride and hydrosulphate forms of porous poly(vinylpyridine) could retain some amines and alcohols. This behaviour suggests that the acid forms of the beads may be useful as a subtractor for amines and alcohols in GC. Several investigations on the subtraction of amines and alcohols have been reported, and include the removal

of amines with phosphoric acid[4] and copper(II) chloride on Chromosorb G[2] and of alcohols with boric acid[5–8], metal hydrides[5] and 3-nitrophthalic anhydride[6].

This paper reports an evaluation of the acid forms of poly(4-vinylpyridine) (4VP) and poly(2-vinylpyridine) (2VP) as subtractors of amines and alcohols in GC. The subtractor columns show less bleeding of acids because the acids are retained as stable salts on the polymer matrix.

EXPERIMENTAL

Apparatus and reagents

A Shimadzu GC-4BMPF gas chromatograph equipped with dual hydrogen flame-ionization detectors was used for the evaluation of the proposed columns. A JEOL JMS-01SG mass spectrometer combined with a JEOL JGC-1100 gas chromatograph was used for the identification of the GC peaks. The gas chromatograph, equipped with a 2 m × 3 mm I.D. glass column, consisting of a subtractive precolumn (0.2 m) and an analytical column (1.8 m, 4VP), was operated at a column temperature of 150°C and the mass spectrometer was operated at an electron energy of 75 eV.

The surface properties and thermal analysis of the polymer beads were studied with the apparatus reported previously[3].

All reagents used were of commercial reagent grade and used without purification.

Preparation of acid forms of poly(vinylpyridine)

4VP and 2VP beads (20% divinylbenzene), which were prepared according to a method described previously[3], were converted into the acid forms by shaking with excess of 1 M hydrochloric or sulphuric acid for 24 h. The resulting products were washed with water and methanol and the 60–80-mesh fraction was used as the column packing.

Gas chromatography

Unless otherwise stated, the columns used were 1 m × 3 mm I.D. glass columns packed with the subtractors, viz., the hydrochloride form of porous 4VP (4VP-HCl), the hydrosulphate form of porous 4VP (4VP-H$_2$SO$_4$), the hydrosulphate form of porous 2VP (2VP-H$_2$SO$_4$) and the hydrosulphate form of gel 4VP (G-4VP-H$_2$SO$_4$). A column (1 m × 3 mm I.D.) packed with 4VP or 2VP was used as a reference column. Nitrogen was employed as the carrier gas at a flow-rate of 60 ml/min and the sample size was 0.2 μl. The percentage removal of compounds was determined by comparing their peak areas on the subtractor acid-form column with those on the reference column. The specific retention volume (per gram of adsorbent), V_m, was calculated according to the equation of Kiselev et al.[9].

RESULTS AND DISCUSSION

The properties of the polymers used are listed in Table I. The surface properties of the porous polymers change markedly on conversion of the free base form into the acid form. The surface area of the acid form is larger than that of the base form,

TABLE I

CHARACTERIZATION OF POLY(VINYLPYRIDINE) BEADS AND THEIR ACID FORMS

Beads	Specific surface area (m^2/g)	Pore volume (cm^2/g)	Average pore diameter (nm)	Elemental analysis (%)		
				N	Cl	S
4VP	34.0	0.205	24.1	8.15	—	—
4VP-HCl	53.0	0.114	8.6	5.52	13.40	—
4VP-H$_2$SO$_4$	58.3	0.074	5.1	5.35	—	6.15
2VP	30.0	0.062	8.2	8.20	—	—
2VP-H$_2$SO$_4$	55.0	0.021	1.5	5.54	—	6.06
G-4VP	0	0	0	7.95	—	—
G-4VP-H$_2$SO$_4$	0	0	0	5.42	—	6.86

and the pore diameter is smaller. In addition, the surface properties of the acid form differ with the counter ions; the hydrosulphate form has a larger surface area than the hydrochloride form. The analytical data in Table I show that no free base is present in the acid form of the polymers.

The thermal stability of polymers is an important factor in their use as packii. s in GC. Thermogravimetric curves for the porous polymers used are shown in Fiġ. ı. In general, the thermal stability of the acid form is lower than that of the free base, and the hydrosulphate form is more stable than the hydrochloride form. The thermal stability of the porous 4VP series decreases in the order 4VP > 4VP-H$_2$SO$_4$ > 4VP-
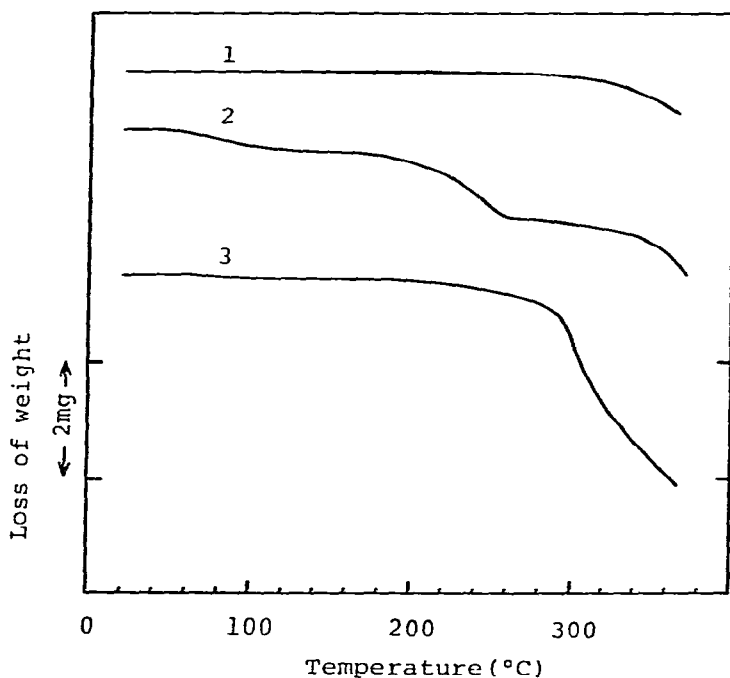

Fig. 1. Thermograms of the porous polymers in a nitrogen atmosphere. (1) 4VP (sample weight, 8.14 mg); (2) 4VP-HCl (8.38 mg); (3) 4VP-H$_2$SO$_4$ (8.26 mg).

HCl, and they are stable up to 290, 183 and 170°C, respectively. With 4VP-HCl, the weight loss corresponding to the liberation of hydrochloric acid was observed at 170–257°C. The weight loss observed with 4VP-HCl and 4VP-H$_2$SO$_4$ at temperatures near 100°C is due to the dehydration of the polymers. The extent of deterioration of the acid form of the columns was determined by measurement of the chlorine or sulphur content of the polymers when heated at 170°C for 100 h under a stream of nitrogen (flow-rate 60 ml/min). A slight decrease in the sulphur content was found with 4VP-H$_2$SO$_4$, but with 4VP-HCl the chlorine content decreased to 67.2% of the initial content. The thermal instability of 4VP-HCl was also demonstrated by the spectral change in the infrared region, where the absorption peak at 1625 cm^{-1} based on the C=N stretching of N-protonated pyridine decreased in size.

The acid form of porous poly(vinylpyridine) beads is able to retain most of the amines by formation of stable salts on the polymers. The percentage removal of the amines with 4VP-HCl, 4VP-H$_2$SO$_4$ and 2VP-H$_2$SO$_4$ is given in Table II. Primary and secondary amines were retained effectively on all three columns, but tertiary amines not. This process is governed by the affinity of amines for acids combined with the basic functional groups on the polymer. Steric factors also must play an important role in salt formation on the polymer matrix. The three polymers show nearly equal affinities for the amines, and the pK_b values of the amines are independent of their reactivity. The reactivity of tertiary amines on the three polymers is lower than that on the phosphoric acid subtractor column reported by Fryčka and Pospíšil[4],

TABLE II

PERCENTAGE REMOVAL OF AMINES BY 4VP AND 2VP ACID-FORM COLUMNS

Compound	pK_b	4VP-HCl column temperature (°C)		4VP-H$_2$SO$_4$ column temperature (°C)		2VP-H$_2$SO$_4$ column temperature (°C)	
		130	150	150	170	150	170
Ethylamine	3.37	100	100	100	100	100	100
n-Propylamine	3.47	100	100	100	100	100	100
n-Butylamine	3.39	100	100	100	100	100	100
Diethylamine	3.02	100	100	100	100	100	100
Di-n-propylamine	3.00	100	100	100	100	100	100
Di-n-butylamine	2.75	100	100	100	100	100	100
Triethylamine	3.33	—	37	53	50	47	47
Tri-n-propylamine	3.35	—	15	3	20	0	7
Tri-n-butylamine	3.11	—	0	0	0	0	9
Isopropylamine	3.37	100	100	100	100	100	100
Isobutylamine	3.57	100	100	100	100	100	100
Isoamylamine	3.40	100	100	100	100	100	100
sec.-Butylamine	3.44	100	100	100	100	100	100
tert.-Butylamine	3.55	100	100	100	100	100	100
tert.-Amylamine	3.05	100	100	100	100	100	100
2-Aminoethanol	4.53	100	100	100	100	100	100
Morpholine	5.60	100	100	100	100	100	100
α-Picoline	7.52	6	0	34	22	43	30
γ-Picoline	8.00	16	0	39	21	46	30
Pyridine	8.81	0	0	16	0	14	2
Aniline	9.42	100	100	100	100	100	100

owing to the difference in reactivity between a packing in which acid groups are fixed to the polymer and a packing in which no acid groups are fixed to the polymer.

It was expected that the flow-rate of the carrier gas would affect the reactivity of amines, but no significant change in the removal of amines was observed when the flow-rate was changed from 60 to 120 ml/min.

The effect of water on the removal of amines was investigated. With 4VP-H$_2$SO$_4$, no significant effect on the removal of primary and secondary amines was observed when a sample containing 95% of water was used. The water, however, affected the life of the 4VP-HCl column; when 4 μl of the aqueous sample was injected twenty times repeatedly, peaks due to the amines that had previously been retained on the column were observed in the later runs.

4VP-H$_2$SO$_4$ and 2VP-H$_2$SO$_4$ but not 4VP-HCl, columns, can retain alcohols effectively, except for *tert.*-butanol (Table III). The removal of alcohols by these columns is based on the formation of sulphuric acid esters. The reactivity of 4VP-H$_2$SO$_4$ with alcohols is higher than that of 2VP-H$_2$SO$_4$, on which some alcohols with bulky alkyl groups show low reactivity. This appears to be the reason for the steric effect, especially with 2VP-H$_2$SO$_4$.

TABLE III

PERCENTAGE REMOVAL OF ALCOHOLS BY 4VP AND 2VP ACID-FORM COLUMNS

Compound	4VP-HCl column temperature (°C)		4VP-H$_2$SO$_4$ column temperature (°C)			2VP-H$_2$SO$_4$ column temperature (°C)		
	130	150	130	150	170	130	150	170
Methanol	0	0	100	100	100	100	100	100
Ethanol	0	0	100	100	100	77	100	100
n-Propanol	0	0	100	100	100	86	99	100
n-Butanol	0	0	100	100	100	64	95	100
Isopropanol	0	0	100	100	100	38	70	99
Isobutanol	0	0	100	100	100	31	56	93
sec.-Butanol	0	0	100	100	100	29	49	90
tert.-Butanol*	26	52	100	100	100	30	47	74
	(26)	(52)	(100)	(100)	(100)	(6)	(21)	(56)

* Percentage removal of *tert.*-butanol was obtained with a 2 m × 3 mm I.D. glass column consisting of a subtractive pre-column (1 m) and an analytical column (1 m, 4VP). The values in parentheses indicate the percentage of dehydration, which was determined by measuring the amount of 2-methyl-1-propene produced from the alcohol.

With *tert.*-butanol, production of 2-methyl-1-propene by dehydration of the alcohol was identified by GC–mass spectrometry (MS). The percentage dehydration of *tert.*-butanol on the three columns is shown in Table III. In the 4VP-H$_2$SO$_4$ column, the alcohol is completely converted into 2-methyl-1-propene, but this dehydration occurs only partially on the other columns. A similar reaction of tertiary alcohols in GC using boric acid[5–8] and 3-nitrophthalic anhydride[6] subtractor columns has been reported.

The reactivity of alcohols with 2VP-H$_2$SO$_4$ increases with increase in the operating temperature. The presence of water in a sample does not significantly affect the removal of alcohols on the 4VP-H$_2$SO$_4$ column, but it does on the 2VP-H$_2$SO$_4$

column, the percent removal of isobutanol at 150°C, for example, shown in Table III, being reduced to 31 % in the presence of 95 % water. These results indicate that the mechanism of the reaction is based on esterification. It is assumed that 4VP-HCl can produce alkyl halides with alcohols, as can 4VP-H$_2$SO$_4$ and 2VP-H$_2$SO$_4$, in the GC process, but no halides were not found, even on examination by GC–MS.

A gel-type polymer (G-4VP-H$_2$SO$_4$) was also investigated. In spite of its similar chemical properties to those of the porous polymers, all of the amines and alcohols tested were hardly retained on the G-4VP-H$_2$SO$_4$ column. This indicates that a suitable porosity and large surface area are essential properties of a polymer sub-tractor in GC.

It has been reported that when boric acid is used as a subtractor of alcohols in GC, sometimes the subtracted compounds eventually bleed off as extremely broad peaks, due to borate esters[6,7]. With the subtractors used in this work, bleeding of subtracted compounds was not observed. A 4VP-H$_2$SO$_4$ column would be particularly useful for samples containing alcohols as a solvent, the peaks of which obscure those of other sample constituents.

Table IV shows the retention data of the compounds not retained on 4VP-HCl, 4VP-H$_2$SO$_4$ and 2VP-H$_2$SO$_4$ columns compared with those on 4VP and 2VP columns. The adjusted retention volume (V_o) of hydrocarbons on the acid form of 4VP or 2VP are lower than those on the free base columns. Kiselev et al.[9] reported that the specific retention volume per gram of adsorbent (V_m) on graphitized carbon black was proportional to its surface area. The values of V_m, however, are independent of the surface area of the polymers.

TABLE IV

RETENTION VOLUMES OF VARIOUS COMPOUNDS AT A COLUMN TEMPERATURE OF 150°C

V_o = Adjusted retention volume; V_m = specific retention volume (per gram of adsorbent).

Compound	4VP		4VP-HCl		4VP-H$_2$SO$_4$		2VP		2VP-H$_2$SO$_4$	
	V_o (ml)	V_m (ml/g)	V_o (ml)	V_m (ml/g)	V_o (ml)	V_m (ml/g)	V_o (ml)	V_m (ml/g)	V_o (ml)	V_m (ml/g)
n-Hexane	36.3	10.8	11.2	3.6	12.3	3.7	17.4	7.5	8.0	3.9
n-Octane	116.4	34.5	23.6	7.6	29.6	8.2	34.2	14.7	10.4	5.1
1-Octene	129.4	38.3	26.7	8.5	30.8	8.5	39.1	16.8	10.4	5.1
Benzene	118.9	35.0	69.6	22.6	35.3	9.9	48.9	20.8	10.0	4.8
Cyclohexane	69.6	20.4	13.6	4.4	13.6	3.8	26.7	11.4	8.0	3.9
Acetone	59.1	17.5	72.0	23.2	39.4	10.9	23.6	10.1	11.0	5.4
Methyl ethyl ketone	103.5	30.7	109.9	35.5	48.7	13.4	33.5	14.4	11.6	5.7
Methanol	61.6	18.2	246.4	79.7	—	—	24.2	10.4	—	—
Ethanol	84.4	25.0	249.5	80.9	—	—	29.2	12.5	—	—
n-Propanol	165.1	48.9	450.9	146.2	—	—	45.3	19.5	21.4	10.5
Isopropanol	93.6	27.8	226.7	73.5	—	—	28.6	12.3	12.2	6.2
n-Butanol	316.0	93.7	788.5	254.9	—	—	75.1	32.2	18.4	9.0
Isobutanol	247.6	73.4	431.2	139.2	—	—	59.0	25.3	11.0	5.4
sec.-Butanol	178.6	53.0	326.5	106.3	—	—	44.1	18.9	10.4	5.1
tert.-Butanol	100.4	29.7	40.0	13.0	—	—	25.5	10.9	9.2	4.5
Pyridine	337.6	100.0	1838.2	593.2	462.0	128.1	111.2	47.7	94.9	46.4
1,2-Dichloroethane	175.6	52.0	223.6	72.1	93.6	25.8	52.8	22.6	18.4	9.0
Ethyl acetate	77.0	22.8	59.6	19.2	27.7	7.6	30.4	13.1	9.8	4.8

Generally the peak resolutions of both the 4VP-HCl and 4VP-H$_2$SO$_4$ columns are lower than that of the 4VP column. Therefore, it is preferable to use 4VP-HCl or 4VP-H$_2$SO$_4$ as a pre-column. An example of the simultaneous use of the 4VP-HCl or 4VP-H$_2$SO$_4$ and the 4VP column is shown in Fig. 2. 4VP-HCl and 4VP-H$_2$SO$_4$ columns subtract the amine and amine/alcohol peaks from their chromatograms effectively, and these compounds are recognized by the absence of their peaks when the chromatogram is compared with that obtained by using the reference column.
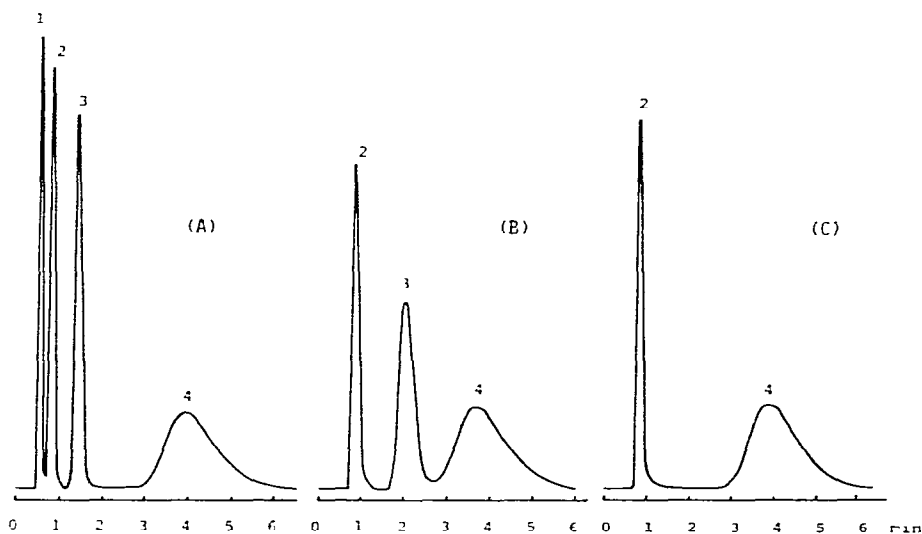

Fig. 2. Chromatograms for a mixture of *n*-propylamine (1), ethyl acetate (2), *n*-propanol (3) and *n*-decane (4). (A) 4VP (80 cm); (B) 4VP-HCl (20 cm) + 4VP (80 cm); (C) 4VP-H$_2$SO$_4$ (20 cm) + 4VP (80 cm). Temperature: 165°C. Column: 1 m × 3 mm I.D.

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