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## NEW SOLID ADSORBENTS FOR THE SEPARATION OF LOWER HYDROCARBONS AND PERMANENT GASES

### I. AMMONIUM TUNGSTOPHOSPHATE

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#### SUMMARY

Ammonium tungstophosphate  $[(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}]$  has been tried as solid adsorbent in gas–solid chromatography for the separation of lower hydrocarbons and permanent gases. The ammonium tungstophosphate (20% on non-porous glass beads) column was tested in the separation of  $\text{C}_1$ – $\text{C}_4$  hydrocarbons in both isothermal and temperature-programmed runs. Ammonium tungstophosphate seems to be an effective solid adsorbent for the separation of methane, ethane, ethylene, acetylene, propane, propylene and butane. The retention times and recoveries were highly reproducible in both isothermal and temperature-programmed runs. The high surface area, ( $>150 \text{ m}^2/\text{g}$ ), uniform pore-size distribution (6–13 Å), uniform particle size distribution, high thermal stability and moderate sorption capacity render ammonium tungstophosphate a potential adsorbent in gas–solid chromatography.

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#### INTRODUCTION

Gas–solid chromatography (GSC) and gas–liquid chromatography (GLC) are extensively used for the separation of wide variety of chemicals and gases. Generally, gases and low-boiling liquids are analysed by GSC and liquids and solids by GLC. Because of the availability of numerous liquid stationary phases, it is usually easy to choose a GLC column for the analysis of particular types of liquids and solids, whereas the selection of a GSC column is limited because of the lack of a large number of solid phases. The solid adsorbents used for the separation of lower hydrocarbons and permanent gases include homogeneously macroporous solids (*e.g.*, xerogels, macroporous glasses), homogeneously microporous solids (*e.g.*, xerogels, microporous glasses, zeolite molecular sieves, carbon molecular sieves, alumina, porous polymers such as Chromosorbs, Porapaks), inhomogeneously porous solids (*e.g.*, xerogels, chalky silica gel) and non-porous solids (*e.g.*, graphitized carbon blacks, aerosil, thermal ungraphitized carbon black<sup>1–12</sup>). Inorganic salts such as NaCl, Zr  $(\text{KPO}_4)_2$  and Zr  $(\text{AsPO}_4)_2$  have also been tried as solid adsorbents for the separation of hydrocarbons<sup>1,13</sup>.

Tailing of peaks is a frequently observed phenomenon in GSC and is attributed mainly to non-linear adsorption, sorption kinetics effects and the sorption capacity of solid adsorbents<sup>1</sup>. The basic requirements for a solid to be used as an adsorbent in GSC are a high surface area, a high thermal stability and a uniform pore size distribution<sup>1</sup>. A new class of microporous solid adsorbent, *viz.*, ammonium tungstophosphate [(NH<sub>4</sub>)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>] appears to be a promising solid phase in GSC. The potential application of this non-siliceous, non-aluminous and non-carbonaceous material stems from its high surface area (nitrogen BET surface area 150–170 m<sup>2</sup>/g), micropores in the range 6–13 Å and high thermal stability (>400°C). The sorption and diffusion of aromatic and saturated and unsaturated aliphatic hydrocarbons and aliphatic alcohols on ammonium tungstophosphate have been reported elsewhere<sup>14–17</sup>. The reported sorption capacity of ammonium tungstophosphate for different organic compounds and the diffusivities of different organic compounds in ammonium tungstophosphate are listed in Table I.

Ammonium tungstophosphate is generally prepared by treating an aqueous solution of 12-tungstophosphoric acid with an aqueous solution of an ammonium salt. Ammonium tungstophosphate, which is a heteropoly oxometallate, is an ionic solid with NH<sub>4</sub><sup>+</sup> cations and a large, cage-like PW<sub>12</sub>O<sub>40</sub> anion often called Keggin structure. The anion has a central phosphorus atom surrounded by four oxygen atoms arranged tetrahedrally. The central tetrahedron is surrounded by twelve octahedra with oxygen atoms at their vertices and tungsten atoms at their centres. The central tetrahedron and the surrounding octahedra are connected by bridging oxygen atoms and each octahedron is connected to its neighbouring octahedra by oxygen atom.

Even though the sorption and catalytic properties of ammonium tungstophosphate and other similar heteropoly oxometallates have been studied in detail, their use in gas chromatography for the separation of hydrocarbons and permanent gases has so far not been reported. This paper describes the potential application of ammonium tungstophosphate for such separations.

## EXPERIMENTAL

Hydrocarbons and gases were supplied by Matheson. Ammonium tungstophosphate was prepared as follows. An aqueous solution of 12-tungstophosphoric acid (BDH) was treated with a stoichiometric amount of ammonium chloride solution. The milky solution thus obtained was concentrated over a water-bath. The ammonium tungstophosphate crystals were separated by centrifugation and washed with distilled water. The solid was dried in an air oven at 110°C for 2 h, then stored in an air-tight bottle.

To prepare the column, 5 g of ammonium tungstophosphate were added to 50 ml of distilled water and stirred until a milky solution was obtained, then 20 g of acid-washed glass beads (0.4 mm diameter) were added. The mixture was stirred continuously and the water was distilled off slowly under vacuum. The ammonium tungstophosphate crystals impregnated on glass beads were dried in an air oven at 110°C for 2 h, then transferred to a stainless-steel 6 ft. × 1/8 in column. GC analyses were carried out with a Hewlett-Packard gas chromatograph fitted with a flame ionization detector and a thermal conductivity detector.

TABLE I

SORPTION AND DIFFUSION OF ORGANIC COMPOUNDS IN AMMONIUM TUNGSTOPHOSPHATE AT 293 K

Type	Sorbate	Sorption capacity (g/g)	Diffusivity $D \times 10^{11}$ (cm <sup>2</sup> /s)
Alcohols <sup>a</sup>	Methanol	0.029	1.0
	Ethanol	0.032	0.7
	1-Propanol	0.040	0.5
	1-Buthanol	0.044	0.4
	2-Methyl-2-butanol	0.030	2.2
	1-Hexanol	0.047	0.05
Aromatics <sup>b</sup>	Benzene	0.028	2.4
	Toluene	0.035	1.3
	<i>p</i> -Xylene	0.021	0.8
	<i>m</i> -Xylene	0.017	0.39
	<i>o</i> -Xylene	0.019	0.45
	Mesitylene	0.014	0.22
	<i>m</i> -Diethylbenzene	0.025	0.13
Saturates <sup>c</sup>	<i>n</i> -Hexane	0.026	4.8
	3-Methylpentane	0.029	4.7
	Cyclohexane	0.027	2.6
	<i>n</i> -Heptane	0.026	4.1
	<i>n</i> -Octane	0.029	2.7
	Isooctane	0.029	2.2
Unsaturates <sup>d</sup>	1-Hexene	0.032	2.9
	2,3-Dimethyl-1-butene	0.026	1.9
	1-Heptene	0.036	2.3
	1-Octene	0.040	0.8
	Cyclohexene	0.033	0.8
	4-Methyl-1-cyclohexene	0.032	1.2

<sup>a</sup> Ref. 17.<sup>b</sup> Ref. 14.<sup>c</sup> Ref. 15.<sup>d</sup> Ref. 16.

## RESULTS AND DISCUSSION

*Separation of C<sub>1</sub>-C<sub>4</sub> hydrocarbons*

Ammonium tungstophosphate seems to be effective for the separation of C<sub>1</sub>-C<sub>4</sub> hydrocarbons. The baseline separation of methane, ethane, ethylene, acetylene, propane, propylene and *n*-butane obtained with the 6 ft. × 1/8 in. ATP column in a temperature-programmed run is illustrated in Fig. 1. The reproducibility of the separation of C<sub>1</sub>-C<sub>4</sub> hydrocarbons was high. The area counts of ethylene, acetylene and propylene were as reproducible as those of methane, ethane, propane and *n*-butane.

In order to evaluate the contribution, if any, from the glass beads, the C<sub>1</sub>-C<sub>4</sub> mixture was injected on to a 6 ft. × 1/8 in stainless-steel column filled with untreated glass beads under identical conditions. It was found that all the C<sub>1</sub>-C<sub>4</sub> hydrocarbons

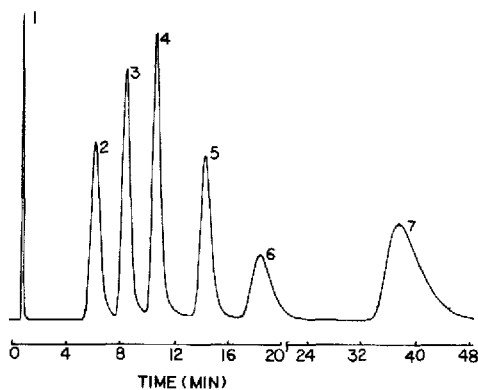


Fig. 1. Chromatogram showing the baseline separation of (1) methane, (2) ethane, (3) ethylene, (4) acetylene, (5) propane, (6) propylene and (7) *n*-butane. Column 6 ft.  $\times$  1/8 in. 20% ammonium tungstophosphate on glass beads; oven temperature, 30°C (4 min); increased at 10°C/min to 100°C, held for 30 min; carrier gas (nitrogen) flow-rate, 7 ml/min; flame ionization detection (FID).

eluted together as one sharp peak. The retention time of this peak was close to that of methane when the same mixture was injected on to the ammonium tungstophosphate column under identical conditions.

An attempt to use ammonium tungstophosphate alone (without glass beads) for the separation of  $C_1$ - $C_4$  hydrocarbons was unsuccessful because the large external mass transfer resistance prevented appropriate flow conditions from being maintained. It was found that the use of glass beads as diluent helped to reduce the pressure drop across the column even though no noticeable contribution from the glass beads towards the separation of hydrocarbons was observed.

#### *Separation of $C_1$ - $C_4$ saturates*

It appears that the separation of methane, ethane, propane and butane can be achieved in a short time by using the ammonium tungstophosphate column. The baseline separation of  $C_1$ - $C_4$  saturates using a 20% ammonium tungstophosphate column in a temperature-programmed run is shown in Fig. 2. The column temperature was initially held at 50°C for 1 min, then increased to 150°C at 10°C/min and held at 150°C for 10 min. The reproducibility of the separation of  $C_1$ - $C_4$  saturates was good. The retention characteristics of  $C_1$ - $C_4$  alkanes in five successive temperature-programmed runs are given in Table II.

The ammonium tungstophosphate column was also tested for its performance in the separation of  $C_1$ - $C_4$  alkanes under isothermal conditions. A baseline separation could be achieved within 15 min by using a 20% ammonium tungstophosphate column at 120°C. A representative chromatogram obtained by injecting a mixture of methane, ethane, propane and *n*-butane is shown in Fig. 3. Even under isothermal conditions the reproducibility of separation was good. The retention characteristics of methane, ethane, propane and *n*-butane in five successive isothermal runs are given in Table III.

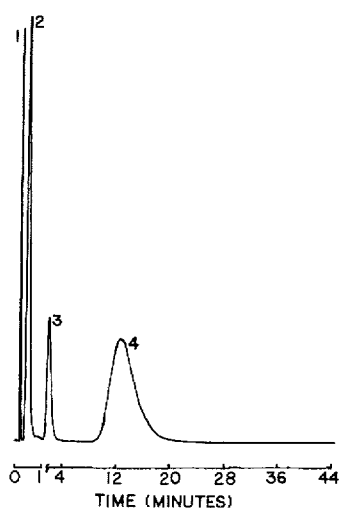
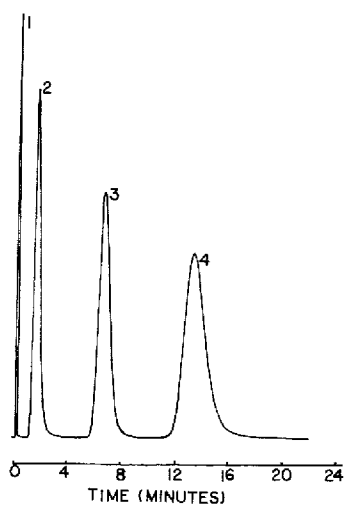


Fig. 2. Chromatogram showing the baseline separation of  $C_1$ - $C_4$  saturated hydrocarbons. Column as in Fig. 1. Oven temperature,  $50^\circ\text{C}$  (1 min), increased at  $10^\circ\text{C}/\text{min}$  to  $150^\circ\text{C}$ , held for 10 min; carrier gas (nitrogen) flow-rate, 20 ml/min; FID. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = *n*-butane.

Fig. 3. Chromatogram showing the baseline separation of  $C_1$ - $C_4$  saturated hydrocarbons under isothermal conditions. Conditions as in Fig. 2 except oven temperature ( $120^\circ\text{C}$ ). Peaks as in Fig. 2.

### Separation of permanent gases

Ammonium tungstophosphate appears to be a promising sorbent for the separation of permanent gases, *viz.*, nitrogen, methane, ethane and carbon dioxide. The separation of permanent gases achieved under isothermal conditions is shown in Fig. 4.

The selective behaviour of the adsorbent towards adsorbated and the peak broadening determine the separating capacity of the column<sup>1</sup>. The elution peaks of lower hydrocarbons and permanent gases obtained with the ammonium tungstophosphate column appear to be sharp and fairly symmetrical and to have a quasi-

TABLE II

RETENTION CHARACTERISTICS OF  $C_1$ - $C_4$  ALKANES OBTAINED BY FIVE SUCCESSIVE TEMPERATURE-PROGRAMMED RUNS WITH A COLUMN (6 ft.  $\times$  1/8 in.) OF 20% AMMONIUM TUNGSTOPHOSPHATE ON GLASS BEADS

Temperature programme:  $50^\circ\text{C}$  (1 min),  $10^\circ\text{C}/\text{min}$  to  $150^\circ\text{C}$ , held for 10 min. Carrier gas (nitrogen) flow-rate, 20 ml/min. Sample size, 0.025 ml.

Hydrocarbon	Mean retention time (s)	Standard deviation (s)
Methane	18.6	0.0
Ethane	104.2	0.4
Propane	399.6	0.7
<i>n</i> -Butane	795.4	0.4

TABLE III

RETENTION CHARACTERISTICS OF C<sub>1</sub>-C<sub>4</sub> ALKANES OBTAINED BY FIVE SUCCESSIVE ISOTHERMAL RUNS WITH A COLUMN (6 ft. × 1/8 in) OF 20% AMMONIUM TUNGSTO-PHOSPHATE ON GLASS BEADS

Column temperature, 120°C; other conditions as in Table II.

Hydrocarbon	Mean retention time (s)	Standard deviation (s)
Methane	12.6	0.0
Ethane	28.8	0.3
Propane	120.6	0.3
<i>n</i> -Butane	792.4	1.7

Gaussian shape. In GSC only ideal conditions produce sharp and symmetrical Gaussian-shaped elution peaks (with peak widths at the inflection point, at half-height and at the base of  $2\sigma$ ,  $2.355\sigma$  and  $4\sigma$ , respectively, where  $\sigma$  is the standard deviation of the peak)<sup>1, 18-20</sup>. Deviations from ideal behaviour are attributed mainly to the inhomogeneous distribution of active sites, non-linear adsorption, diffusional effects and stronger specific interaction of adsorbate molecules with the active sites. For a particular adsorbent, the interaction of an adsorbate molecule with an active site depends mainly on the molecular weight, molecular geometry and electron density of the adsorbate molecule. Even if the distribution of active sites is uniform (Gaussian), the adsorption is linear and the interaction of the adsorbate with the adsorbent is weak, peak broadening can still occur as diffusional effects in a real column cannot be eliminated completely. The effects of diffusion can only be minimized by using small adsorbent particles of uniform size and shape distributed uniformly in a column, by selecting a heavier carrier gas and by reducing the column diameter<sup>1, 18-20</sup>. The ammonium tungstophosphate crystals obtained by treating an aqueous solution of 12-tungstophosphoric acid with ammonium chloride solution seem to have a fairly uniform size. A scanning electron micrograph of these crystals is shown in Fig. 5. As there is a small number of smaller and larger crystals and as the rate of sorption is

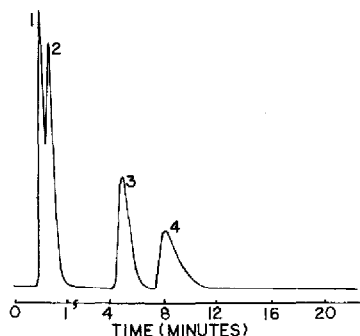


Fig. 4. Separation of permanent gases under isothermal conditions. Column as in Fig. 1. Oven temperature, 35°C; carrier gas (helium) flow-rate, 10 ml/min; thermal conductivity detection. Peaks: 1 = nitrogen; 2 = methane; 3 = ethane; 4 = carbon dioxide.

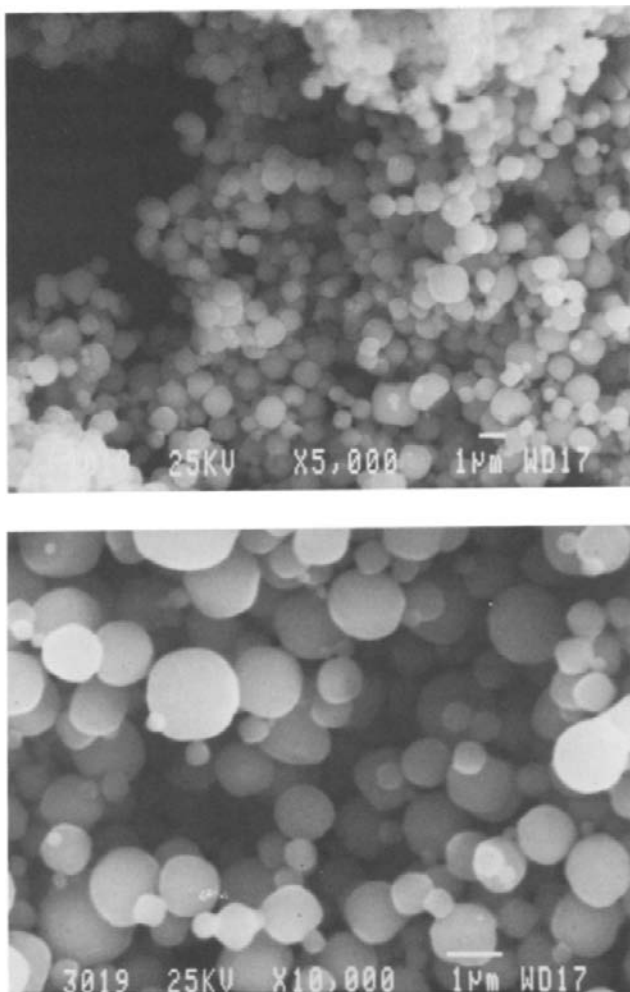


Fig. 5. Scanning electron micrograph of ammonium tungstophosphate crystals.

inversely proportional to the square of the crystal radius, some degree of peak broadening, as in any real column, is to be expected. The fairly symmetric peaks for  $C_1$ - $C_4$  hydrocarbons show that the peak broadening due to an inhomogeneous active site distribution and non-linear adsorption is small. It appears that the fairly uniform particle size distribution, pore size distribution (6-13 Å) and high surface area make ammonium tungstophosphate an effective adsorbent in GSC.

GSC, introduced by Martin and Synge<sup>21</sup>, is widely been used as a reliable method for the separation of hydrocarbons and permanent gases. Since Golay's introduction of capillary columns for high-resolution gas chromatography<sup>22</sup>, much interest has been shown in extending the use of solid adsorbents to capillary chromatography. As the ammonium tungstophosphate packed column is capable of separat-

ing light hydrocarbons and permanent gases, a porous-layer open-tubular (PLOT) column containing ammonium tungstophosphate, by virtue of its high resolving power, should certainly find wide application in GSC.

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