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## USE OF A MODIFIED TENAX GC\* COLUMN PACKING FOR THE DIRECT GAS CHROMATOGRAPHIC ANALYSIS OF PHENOLS IN WATER AT THE PPM LEVEL

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### SUMMARY

Dilute solutions of phenols in water at the ppm level may be analysed gas chromatographically by direct injection onto a column with a packing similar to that used in the Viking 1975 spacecraft: Tenax® GC (2,6-diphenyl-*p*-phenylene oxide polymer) modified with polymetaphenyl ether liquid phase to eradicate irreversible adsorption. Symmetrical peaks were observed for injections of less than 1 ng of phenol and some of its alkylated derivatives. Chromatographic properties of modified Tenax GC columns are reported along with their application to the analysis of some industrial effluents without previous work-up.

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### INTRODUCTION

The presence of phenols in industrial effluents even at the ppm level when discharged into sewerage systems presents particular problems because of toxicity to percolating-filter and activated-sludge organisms, and the characteristic and unpleasant taste imparted to water if used for domestic purposes after reprocessing. Analysis of dilute aqueous solutions of phenols generally involves a lengthy procedure with extraction and concentration steps (ref. 1 and references therein, and refs. 2 and 3). Moreover, spectrophotometry does not distinguish between the many phenols which may be present<sup>†</sup>, and in any case chromogenic reagents have different effects on these<sup>†</sup>.

The requirement of a rapid method, involving no work-up, and identification

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\* Tenax® GC is a registered trademark of Tenax B.V., Arnhem, The Netherlands.

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of individual phenols to determine if an effluent must be diverted led us to investigate gas chromatographic methods. Direct analysis of water samples for contaminants at the ppm level has been reported<sup>5,6</sup>, but for phenol and its derivatives, columns with packings such as Free Fatty Acid Phase on Chromosorb W were required on which water gave a large interfering peak. In analyses of this kind the elution of water may constitute a particularly serious problem since irreversible adsorption on conventional support materials can give tailing and consequent interference. The use of polytetrafluorethylene as a support material represents a partial solution, but introduces practical difficulties because of its thermoplasticity, and also its hydrophobic character which makes coating with stationary phases difficult.

However, the use of porous polymers as column packing materials for gas chromatography<sup>7</sup> has greatly facilitated the analysis of mixtures of polar compounds. Porous beads of polystyrene or of copolymers of styrene and divinylbenzene may be used for the analysis of aqueous solutions, since water is quickly eluted and does not interfere with other adsorbed compounds. On the other hand analyses are restricted to fairly low-boiling compounds by the long retention times and fairly low temperature limits of operation.

These restrictions make the more usual porous polymers inapplicable in the analysis of phenols, so that the recent commercial availability of the highly thermostable 2,6-diphenyl-*p*-phenylene oxide polymer (Tenax GC) has invoked considerable interest, especially in view of its very low affinity for water which is thus eluted without either adsorption or interference with the sorption of other compounds<sup>8</sup>. Tenax GC has found wide application in the pre-column concentration of trace organics in air and in the headspace of biomedical samples, and analytical aspects of the method have been investigated<sup>9,10</sup>. There have also been some reports of the use of Tenax GC as a column packing<sup>9,11</sup>, in spite of the observation of irreversible adsorption<sup>9</sup>, and the material has been recommended for the separation of a number of high-boiling compounds<sup>12,13</sup>. Polar compounds are eluted at relatively low column temperatures compared to other porous polymers<sup>13</sup>.

In this paper we report the analysis of very dilute aqueous solutions of phenols on a gas chromatographic column packing similar to that originally developed<sup>14</sup> for the study of the Martian surface in the Viking 1975 spacecraft. This column material, Tenax GC modified with polymetaphenyl ether liquid stationary phase, provides<sup>14</sup> efficient transmission and resolution of ng quantities of organic compounds in the presence of million-fold excesses of water.

## EXPERIMENTAL

The gas chromatograph was a Perkin-Elmer 900, with 6 ft.  $\times$  1/8 in. I.D. stainless-steel columns. Column packings were: (i) Tenax GC (Field, Richmond, Great Britain) as received; (ii) Tenax GC modified by stirring 1.85 g with 2% of its weight (0.037 g) of polymetaphenyl ether OS 138 (Phase Separations, Queensferry, Great Britain) dissolved in 20 ml ethyl acetate. The solid was filtered off, and dried overnight in an oven at 50°; and (iii) Tenax GC (1.85 g) modified as above but with 5% of its weight (0.0925 g) polymetaphenyl ether in 50 ml ethyl acetate.

Columns, packed by gentle mechanical vibration with suction, were conditioned at room temperature for 1 h, and then raised to 300° (250° for modified

Tenax GC columns)) at 8°/min and held at the maximum temperature for 1 h. Nitrogen was used as carrier gas. Injection and manifold temperatures were 230 and 250°, respectively.

## RESULTS AND DISCUSSION

### *Chromatography of phenols on unmodified Tenax GC*

The strong irreversible adsorption of polar compounds on Tenax GC has previously been demonstrated; the effect was especially marked for 2-ethylphenol, and injections of as much as 100 ng were necessary before significant signals could be observed, unless the column was first "primed" with 1-octanol<sup>9</sup>.

Adsorption effects on Tenax GC were first confirmed in this work from the measurements summarised in Table I of peak asymmetry<sup>15</sup> (*P*)—the ratio of the total baseline intercept to twice the baseline intercept of the leading part of the peak—for phenol and three of its alkyl derivatives.

TABLE I

PEAK ASYMMETRY<sup>15</sup> (*P*) AND AREA (*A*) FOR FOUR PHENOLS INJECTED ONTO COLUMNS OF MODIFIED AND UNMODIFIED TENAX GC

<i>Phenol</i>	<i>Tenax GC</i>		<i>Tenax GC modified with a solution containing 2% of its weight of polymetaphenyl ether</i>		<i>Tenax GC modified with a solution containing 5% of its weight of polymetaphenyl ether</i>	
	<i>P</i>	<i>A (mm<sup>2</sup>)</i>	<i>P</i>	<i>A (mm<sup>2</sup>)</i>	<i>P</i>	<i>A (mm<sup>2</sup>)</i>
Phenol	1.75	342	1.08	595	1.05	654
<i>m</i> -Cresol	1.39	264	1.27	468	1.08	508
2,3-Xylenol	2.27	234	1.14	384	1.09	438
3-Ethyl-5-methylphenol	3.33	352	1.15	672	1.06	670

### *Modification of Tenax GC*

Attempts were now made to deactivate the adsorption sites by treatment with a dilute solution of polymetaphenyl ether (six rings per molecule). This liquid phase was chosen<sup>14</sup> because of its high temperature stability, and the similarity of its molecular structure to that of Tenax GC.

A marked improvement in peak symmetry was observed after treatment of the Tenax with 2% of its weight of the liquid phase, and the areas of the peaks also increased relative to the unmodified polymer for injections of the same weights of the test phenols (Table I). But only treatment with a more concentrated solution of polymetaphenyl ether (5% of the weight of Tenax) gave nearly symmetrical peaks; a further increase in peak areas was also observed (Table I). Moreover, graphs of peak area against weight injected (Fig. 1) were linear and passed through the origin for solutions of phenol, *m*-cresol, and 2,6-xylenol on the 5% modified Tenax GC, in contrast to observations for the unmodified and unprimed polymer<sup>9</sup>.

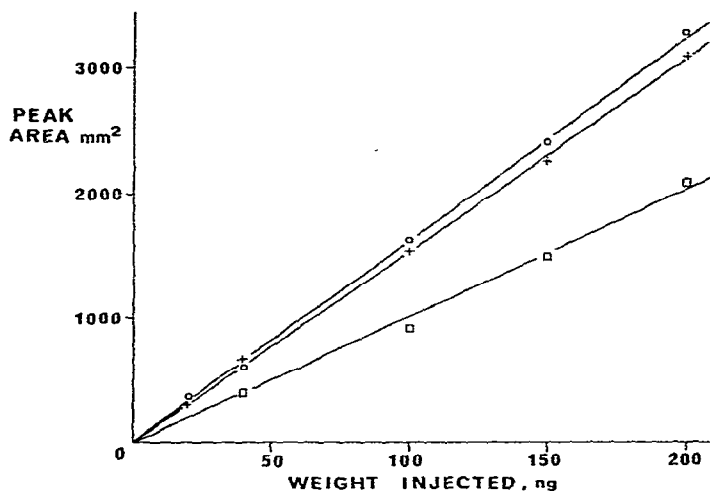


Fig. 1. Graphs of peak area against weight chromatographed for phenols injected as dilute aqueous solutions onto a 6 ft.  $\times$  1/8 in. I.D. stainless-steel column packed with Tenax GC, modified with a solution containing 5% of its weight of polymetaphenyl ether, at 190°.  $\square$ , Phenol; +, *m*-cresol;  $\circ$ , 2,6-xyleneol.

Retention times ( $t_R$ )\* were shorter for the phenols on the Tenax GC modified with 2% polymetaphenyl ether than on the unmodified material, but were extended on the 5% modified polymer (Fig. 2), which apparently shows a combination of gas-solid and gas-liquid chromatographic properties. Graphs of  $\log t_R$  against boiling point were linear (Fig. 2) but with some scatter for compounds with sterically hindered OH groups, *e.g.*, 2,6-xyleneol. Retention times on the 5% modified column are listed in Table II: among phenol and its mono- and dimethyl derivatives, only the *m*- and *p*-cresol, and 2,4- and 2,5-xyleneol pairs are not resolved.

Van Deemter plots were constructed\* for phenol on the unmodified and 5% modified Tenax GC (Fig. 3). A considerable improvement is shown in both apparent plate number and dependence of HETP on flow-rate for the modified polymer. Repeated use of the 5% modified Tenax GC resulted in only a small change in HETP (Fig. 3).

#### *Direct analysis of aqueous industrial effluents for phenols*

Analysis of dilute aqueous solutions of phenols by injection onto a column of Tenax GC modified with a solution of 5% of its weight of polymetaphenyl ether showed that symmetrical peaks with an acceptable signal-to-noise ratio could be obtained below the 1 ppm level. A chromatogram obtained from 0.2  $\mu$ l of an aqueous solution containing 2 ppm (*i.e.*, 400 pg) of each of phenol, *p*-cresol, and 2,5-xyleneol is illustrated in Fig. 4.

\* Retention times<sup>9,13</sup> and HETP values<sup>13</sup> on Tenax GC have been reported to depend on the weight of compound injected above approximately 1  $\mu$ g. In this work, therefore, the weights were kept below this limit.

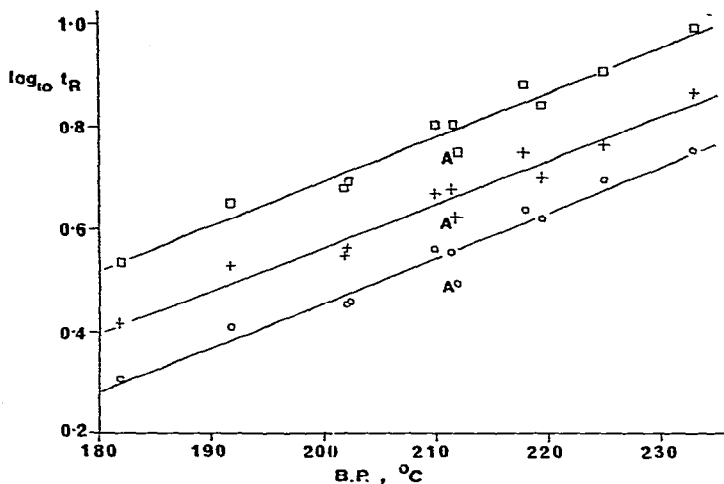


Fig. 2. Graphs of  $\log_{10}(t_R, \text{min})$  against boiling point for a series of alkyl phenols on Tenax GC in 6 ft.  $\times$  1/8 in. I.D. stainless-steel columns. +, Unmodified Tenax GC at 210° (carrier flow-rate, 14 ml/min); ○, Tenax GC, modified with a solution containing 2% of its weight of polymetaphenyl ether, at 190° (carrier flow-rate, 20 ml/min); and □, Tenax GC, modified with a solution containing 5% of its weight of polymetaphenyl ether, at 190° (carrier flow-rate, 20 ml/min). Points for 2,6-xyleneol marked A.

TABLE II

RETENTION TIMES,  $t_R$ , FOR PHENOL AND TEN ALKYL DERIVATIVES

Column, 6 ft.  $\times$  1/8 in. Tenax GC modified with a solution of 5% of its weight of polymetaphenyl ether at 190°; flow-rate, 20 ml/min.

Compound	$t_R$ (min)
Phenol	3.45
<i>o</i> -Cresol	4.50
<i>m</i> -Cresol	4.88
<i>p</i> -Cresol	4.90
2,6-Xylenol	5.65
2,4-Xylenol	6.40
2,5-Xylenol	6.40
3,5-Xylenol	7.05
2,3-Xylenol	7.75
3,4-Xylenol	8.20
3-Ethyl-5-methylphenol	9.95

Industrial effluent samples were now chromatographed (Fig. 5) by direct injection of up to 1  $\mu\text{l}$  onto the modified Tenax. Constituent phenols were identified from comparisons of  $t_R$ , while quantitative analyses were made (Table III) from calibration graphs of the type shown in Fig. 1. For one effluent, samples were analysed at three stages of treatment. The marked reduction in the content of phenol and cresols after the first treatment only is clear. The suitability of these effluents' entering the sewerage system can thus be judged extremely rapidly and without prior work-up.

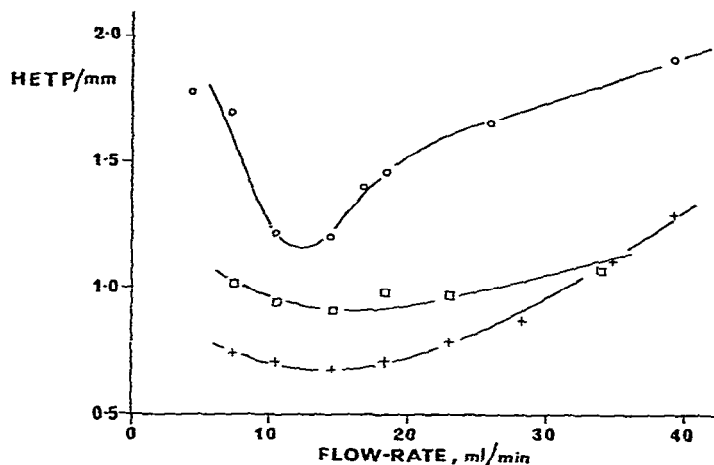


Fig. 3. Van Deemter plots for phenol on Tenax GC in 6 ft.  $\times$  1/8 in. I.D. stainless-steel columns.  $\circ$ , Unmodified Tenax GC at 210°; +, Tenax GC modified with a solution containing 5% of its weight of polymetaphenyl ether, at 190°; and  $\square$ , as in the latter but after repeated use of the column.

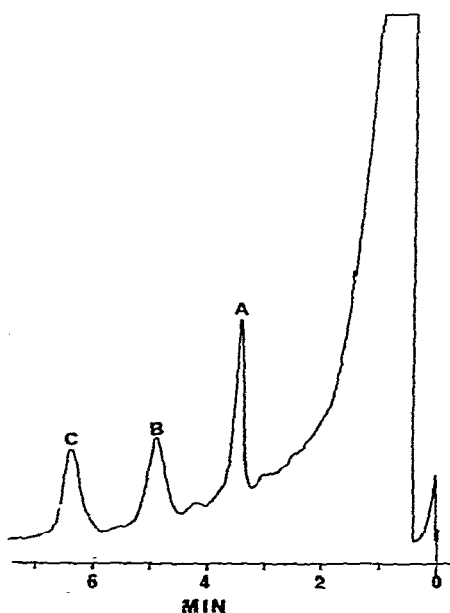


Fig. 4. Chromatogram from 400  $\mu$ g each of (A) phenol, (B) *p*-cresol, and (C) 2,5-xyleneol injected as a 2 ppm solution in water onto a 6 ft.  $\times$  1/8 in. I.D. stainless-steel column containing Tenax GC modified with a solution containing 5% of its weight of polymetaphenyl ether, at 190°.

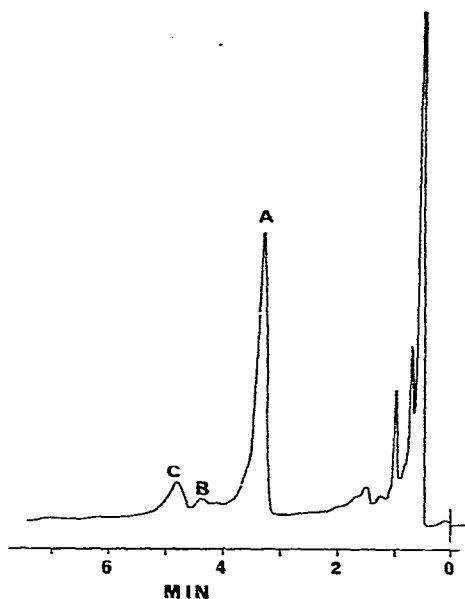


Fig. 5. Chromatogram of 0.5  $\mu$ l of an industrial effluent. Column as in Fig. 4. A = Phenol; B = *o*-cresol; C = *m*- + *p*-cresol.

TABLE III

ANALYSES OF INDUSTRIAL EFFLUENTS FOR PHENOLS ON A MODIFIED TENAX GC COLUMN AT 190°

Phenol	Effluent A (ppm)	Effluent B (ppm)	Effluent C		
			Original* (ppm)	After first treatment (ppm)	After second treatment (ppm)
Phenol	8	4	120	2	2
<i>o</i> -Cresol	—	<1	12	<1	<1
<i>m</i> + <i>p</i> -Cresol	—	—	18	≪1	≪1
2,6-Xylenol	—	4	—	—	—
3,5-Xylenol	—	12	—	—	—
3,4-Xylenol	—	8	—	—	—

\* See Fig. 5.

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