The Direct-Injection GLC Analysis of Xylenols in Industrial Wastewaters

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The direct aqueous injection GLC analysis of phenol, the cresol isomers, chlorophenol isomers and dichlorophenol isomers in wastewaters using 4% dinonylphthalate on Chromosorb G has been reported by this laboratory (BAIRD, *et al*, 1974). The characteristics of this column were briefly compared to other GLC methods for the analysis of phenolics (*e.g.* BAKER 1966; BAKER and MALO, 1967) in aqueous systems, and it was found to be more suitable for the determination of the phenolics of interest. Since then, we have found that the analysis of xylenol (dimethylphenol) isomers in the discharges of certain petroleum industries can be useful for the characterization and fingerprinting of these wastes downstream from the point of discharge, up to, and including the point of influence to wastewater treatment facilities. The analysis of these compounds may also help determine which process or part of the industrial plant is responsible for the discharge.

The purpose of this note is to give the analytical conditions under which the xylenols may be determined along with other phenolics for the characterization of petroleum waste discharges using the dinonylphalate columns.

Experimental

All GLC work was performed on a Perkin-Elmer Model 900 gas chromatograph equipped with dual FID and dual columns. The detectors were operated with H_2 and air pressures of 20 psi and 30 psi, respectively. Columns were 4% dinonylphthalate on 80/100 mesh Chromosorb G, 2m x 3 mm Pyrex glass. The columns were preconditioned for 24 hours at 175°C. Injector port, manifold and column temperatures were 175°C, 175°C and 140°C, respectively, for sample analyses. Ultra pure N_2 (Linde) was used as the carrier gas at 40 psi and a flow rate of 60 ml/min. Phenol and cresol standards were prepared in aqueous solution from the pure Eastman Organic Co. reagents. The xylenols were obtained

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from Polyscience Corp. as 10% xylenols in benzene, and were prepared as standards by dilution in a 1% methanol/water system.

Standards and some samples were analyzed by direct aqueous injection. Oily, and highly concentrated samples require dilution and homogenization with distilled water and/or methanol. Results were quantitated by peak height analysis.

Discussion

Table I exhibits relative retention, calibration, and boiling point data for phenols, the cresols, and xylenols obtained under the conditions described above.

TABLE I

Relative Retention and Calibration Factors for Phenol, Cresols and Xylenols on a 2m, 4% Dinonylphthalate Column, 140°C Oven Temperature

Compound	r	f	b
phenol	1.00	14.8	182
o-cresol	1.35	18.3	192
p-cresol	1.70	17.4	202
m-cresol	1.75	17.4	203
2,3-xylenol	2.84	28.4	218
2,4-xylenol	2.32	17.9	211
2,5-xylenol	2.33	17.9	242
2,6-xylenol	1.51	31.2	212
3,4-xylenol	3.45	24.0	225
3,5-xylenol	3.09	31.3	219

r = Relative retention
f = Calibration factor, ng/sq. in., chart speed = 5 mm/min., 1 mv span, range = 1, attenuation = 1
b = Boiling point, °C

Figure I is a chromatogram of a mixed standard of these materials, showing the resolution and peak shapes yielded by the 2m column. It should be noted that some of the columns prepared gave a degree of resolution for *m*-cresol and *p*-cresol, while others provided none. Previous work at 125°C (BAIRD, *et al*, 1974) never gave resolution of these two isomers. No resolution of the 2,4- and 2,5-isomers of xylenol was achieved, even with temperature programming, perhaps due to their steric similarity.

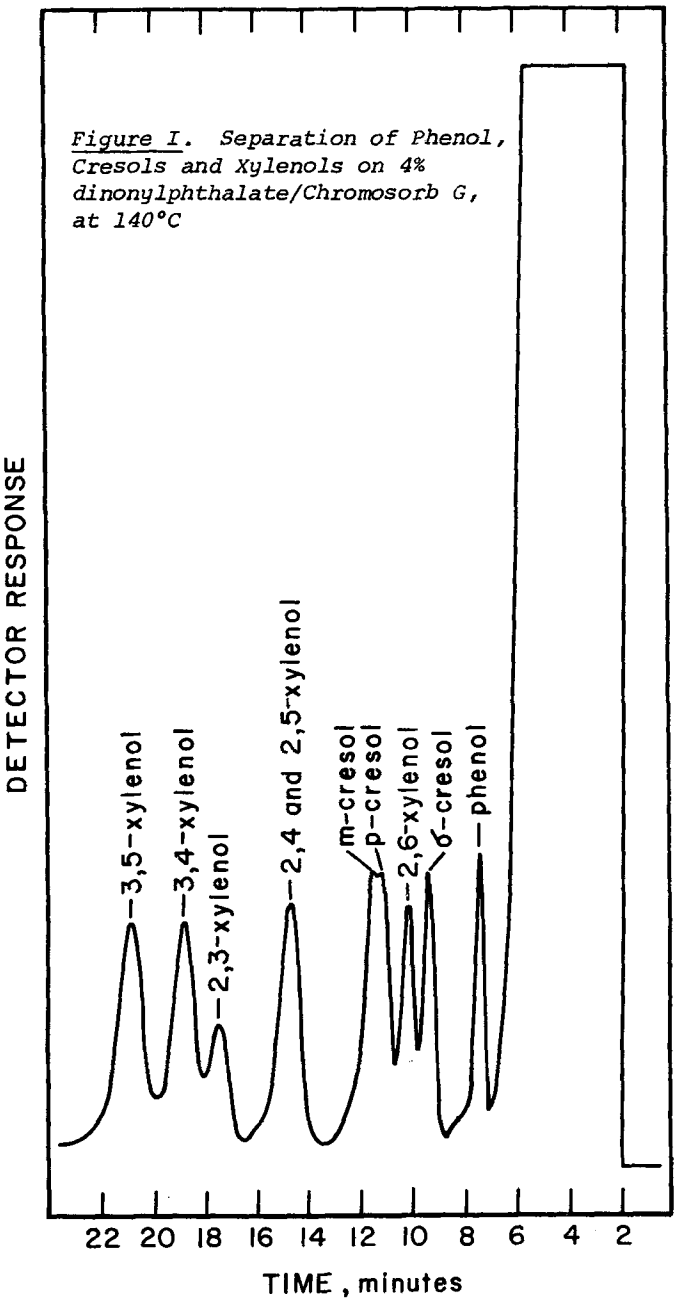

Figure I. Separation of Phenol, Cresols and Xylenols on 4% dinonylphthalate/Chromosorb G, at 140°C

Table II exhibits phenol data collected from two different refineries, and trunk sewer sampling stations downstream from the refineries. Since only one of the plants was discharging phenolics at the time of sampling, it was relatively easy to trace the origin of heavy phenolic pollution to Industry number 2. When both Industry numbers 1 and 2 are discharging significant levels of phenolic wastes, it becomes

just as easy to differentiate between the two when xylenols are analyzed, since Industry number 1 is not a known discharger of xylenols.

TABLE II

Analysis of Some Petroleum Industry Discharges and Sewer Trunk Line Stations for Phenolics

Constituent/ Concentration (mg/l)	Sample No/Type					
	7252 Ind #1 Dis-charge	7276 Ind #2 Dis-charge	7236 Trunk Down-stream	7253 Trunk Down-stream	7753 Ind #2 Dis-charge	7766 Trunk Down-stream
phenol	0.88	3016	2165	20.3	3820	78.7
o-cresol	ND	5842	118	21.8	415	34.2
m-cresol	0.75	{56	{185	{36.3	452	19.5
p-cresol	ND				484	17.9
2,3-xylenol	ND	8177	70.2	17.3	ND	ND
2,4- & 2,5-xylenol	ND	963	44.5	20.0	926	194
2,6-xylenol	ND	1547	93.9	29.3	371	82.2
3,4-xylenol	ND	ND	ND	ND	147	100
3,5-xylenol	ND	ND	ND	ND	1340	ND

ND - Not Detected

References

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