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Note

Gas chromatographic determination of phenols in waste water–oil emulsions

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Phenols are common pollutants in wastes arising from the petrochemical industry or any other industry involving large amounts of kerosene[1], oil, naphtha or coal. Based on many years' experience in this Laboratory, it has been observed that the concentration of phenols in some of the samples coming from such industries exceeds by several orders of magnitude the permitted level for liquid wastes.

A standard procedure[2] for the determination of phenols involves steam distillation, extraction of the distillate with chloroform and spectrophotometric determination. The method is suitable for volatile phenols, *i.e.*, phenol, cresols, xylenes, guaiacol, thymol and some chloro derivatives. Some of the phenols, however, particularly nitro-substituted[3] derivatives, cannot be recovered by steam distillation. In addition, phenols with *para* substituents do not give a colour reaction with the 4-aminoantipyrine reagent used in spectrophotometric determination. As a consequence, the results of such a determination might be low.

Incineration is the usual procedure for eliminating organic wastes composed of deteriorated oil and emulsions used in metal manufacturing. However, burning wastes containing significant amounts of phenols can result in dangerous gaseous pollutants, so careful determination of phenol species prior to incineration is needed. As the spectrophotometric determination of phenols in water–oil mixtures is difficult and of low precision, and the complexity of the samples together with low individual phenol concentrations prevents direct gas chromatographic (GC) determination, this paper reports an attempt to solve the problem of the determination of phenol by extraction and GC.

EXPERIMENTAL

A Spectra-Physics 7100 research gas chromatograph equipped with a flame ionization detector, an autosampler adjusted to inject 2 nl and an integrator was employed. A fused-silica 20 m × 0.23 mm I.D. Supelco SPB 5 capillary column and purified hydrogen as carrier gas were used throughout. The following chromatographic conditions provided a baseline separation of fourteen standard phenols: initial temperature 40°C for 10 min, increased at 5°C/min to 70°C, held for 1 min, a second ramp at 8°C/min to 200°C and isothermal operation for the next 10 min. All

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the phenols were eluted in 35 min, but the final ramp of 15°C/min and the hold of 10 min were necessary to elute heavy components from the oil extracts. The column head pressure was maintained at 40 kPa and the injector was operated at 250°C in the splitless mode for 0.5 min, then the splitting ratio automatically regained its original value of 1/200.

Fig. 1a shows the separation of the standard phenol mixture. Depending on the type of the phenol analysed, and with the instrument operating at maximum sensitivity, the detection limits varied from 2 to 5 mg/l in direct determinations.

Materials

All the organic compounds were of analytical-reagent grade and used as received. For recovery experiments, doubly distilled water was used. Phenols were used without further treatment; the stock solutions in ethanol were kept refrigerated. No noticable deterioration of the constituents was observed during a period of 4 weeks.

Stock standard solutions

A stock solution containing approximately 100 ppm of each of the phenols was prepared by mass, and for detector calibration diluted portions (10, 20 and 50 ppm) were used. The following phenols were used (in order of elution): 2-chlorophenol, phenol, 2-methylphenol, 2-nitrophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, hydroquinone, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, 2,4-dinitrophenol, 3-nitrophenol, 4-nitrophenol, 2,3-dinitrophenol and benzylphenol. The plot of detector response *vs.* individual phenol concentration was linear, with a regression coefficient exceeding 0.99.

RESULTS AND DISCUSSION

Liquid wastes originating from a car engine factory contained two phases: a grey aqueous layer, apparently a fine water-oil emulsion, and a dark oil overlayer. In addition, considerable amounts of insolubles and graphite particles were present. The existence of phenols in both phases seemed very probable, especially as the aqueous phase was close to neutral, enabling water-soluble phenates to be formed.

Direct GC analysis of phenols present in such an oil sample is complicated for several reasons. First, a specimen displaying several hundred partially resolved peaks is too complex to permit confident component identification based on GC measurements only. Second, it is likely that some of the heavy components of the wastes are retained permanently in the capillary column, resulting in rapid column deterioration. Finally, the column might be easily clogged with particles from the used oil. Obviously, prior to the determination of phenols, they must be extracted from the complex sample such as a water–oil emulsion, various types of competitive adsorptions may occur and cause interferences. As an alternative, we used an extraction–concentration step and at the same time a clean-up procedure for treating the samples.

Extraction step

Extraction was performed in separating funnels as follows. (1) With the oil layer, the phenols were transferred into the aqueous phase as phenates using equal

volumes of oil and 2.5% sodium hydroxide solution, followed by phase separation. (2) The aqueous water phase, either from the sample or oil extract produced as indicated above was acidified using phosphoric acid. Phosphoric acid was selected rather than hydrochloric or nitric acid. For acidification of the aqueous, as the latter acids may cause oxidation or phenol degradation[4]. (3) The final step consists in phenol extraction with the chosen extractant, phase separation and drying of the organic layer prior to GC analysis using a few pellets of calcium chloride.

To verify the procedure, fresh unused motor oil was employed. GC analysis under the selected conditions (see Experimental) showed that all the phenols are eluted well before the first component of the oil. Prior to the experiments, fresh motor oil was washed with alkali to remove phenols possibly present. The purified oil was then used to study the recovery of phenols from a new oil and the water–oil phase.

Recovery from the oil phase

New oil was doped with known amounts of phenols and the above extraction scheme was followed.

Following step 1, the aqueous phase containing the phenols as phenates was washed twice with equal volumes of light petroleum (b.p. 40–70°C) to remove any residual oil hydrocarbon. In step 3, diethyl ether, benzene and butyl acetate were selected as extractants. As the extraction of phenols with organic solvents is dependent on the degree of dissociation, *i.e.*, the pH of the aqueous phase, experiments on the extraction of phenols with various acidities of the aqueous phase were performed. In the pH range 1.2–5.2 the extraction of phenols with the above solvents was nearly complete, with recoveries from 95 to 102%, except for 2-chlorophenol (78%) and phenol (76%). The percentage extraction is independent of the extractant applied, varying by only 2% about the average. This was calculated to be the overall precision of the extraction–chromatographic procedure.

Recovery of phenols from water–oil emulsion

To prepare a synthetic water–oil emulsion, 10 ml of alkali-washed fresh oil was added to 500 ml of distilled water and mixed vigorously with a mechanical stirrer until an emulsion with slow phase separation was obtained. The prepared sample was enriched with 5–10 ppm of 2-methylphenol, 2-chlorophenol, 2-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 2,3-dinitrophenol, 4-nitrophenol and benzylphenol, made alkaline and washed three times with light petroleum to remove the added oil. The first portion of the light petroleum wash was saved for subsequent GC analysis. The water layer was acidified and extracted with 20 ml of diethyl ether (organic to aqueous phase ratio 1 : 25 and the extract was analysed for phenols recovery.

The resulting chromatogram of the diethyl ether extract is shown in Fig. 1b, revealing the absence of benzylphenol and the recovery of all other components with 95–102% efficiency. A similar efficiency was reported by Abrahamsson and Xie[5] for the extraction of numerous phenols from water with *n*-hexane. A high recovery is maintained provided that the phase ratio does not exceed approximately 1 : 30; at higher phase ratios the extraction is poorer[6].

Fig. 1c shows the chromatogram of the first light petroleum wash with an easily recognized benzylphenol peak, the only phenol extracted with light petroleum from aqueous alkali media.

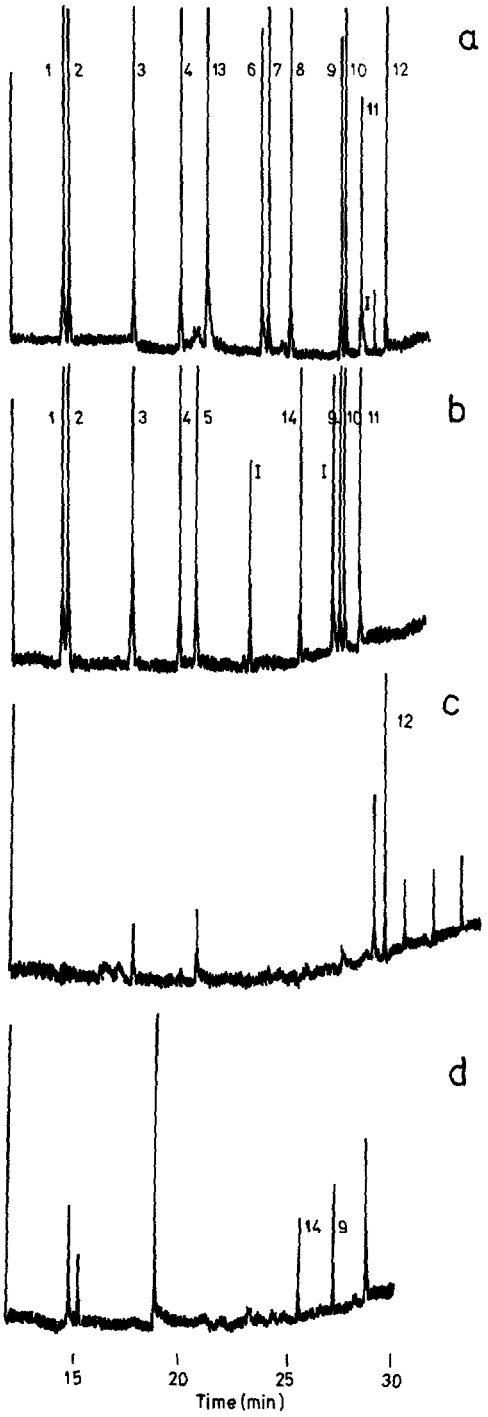

Fig. 1. Chromatograms of (a) standard phenols (50 ppm of each), (b) diethyl ether extract from synthetic water–oil emulsion, (c) light petroleum wash and (d) diethyl ether extract of water–oil emulsion sample I. Detector, flame ionization, $1 \cdot 10^{-12}$ a.u.f.s.; chart speed, 0.1 cm/min from 0 to 14 min, then 1 cm/min. Phenols: 1 = 2-chloro-; 2 = phenol; 3 = 2-methyl-; 4 = 2-nitro-; 5 = 2,4-dichloro-; 6 = hydroquinone; 7 = 4-chloro-3-methyl-; 8 = 2,4,6-trichloro-; 9 = 3-nitro-; 10 = 4-nitro-; 11 = 2,3-dinitro-; 12 = benzyl-; 13 = 2,4-dimethyl-; 14 = 2,4-dinitro-.

TABLE I

DETERMINATION OF PHENOLS (ppm) IN WASTE OIL–WATER EMULSION USING VARIOUS EXTRACTANTS

Phenol	*Sample I*			*Sample II*		
	Diethyl ether	*Benzene*	*Butyl acetate*	*Diethyl ether*	*Benzene*	*Butyl acetate*
3-Nitro-	0.4	18.6	17.9	0.7	17.7	18.0
2,4-Dinitro-	1.7				0.5	0.4
2,4-Dimethyl-	1.7	33.9	29.2	1.2	22.1	20.2
Benzyl-		0.2	0.4			0.4
2,4,6-Trichloro-			0.4			1.1
4-Nitro-			3.2			1.6
Total phenols	2.1	52.7	51.1	1.9	40.3	41.7
Spectrophotometric determination of total phenol content (mg/l)		0.42			0.64	

Sample analysis

The waste samples were split into an emulsion phase (here termed aqueous) and an oil phase, each treated independently according to the previously described procedure. GC analysis of the oil extracts using diethyl ether, benzene or butyl acetate as extractant did not reveal any of the phenols studied here. However, the chromatograms were too complicated in every instance, even with diethyl ether, showing a large number of peaks. Evidently they represent water-soluble organics such as alcohols and acids, and some of the hydrocarbons retained in the aqueous phase owing to poor phase separation and especially to the presence of small organic droplets in water, residual film on the funnel walls, etc. Hence, a positive identification of phenols in oil samples remains a difficult task requiring more sophisticated techniques such as GC combined with mass spectrometry.

After the light petroleum pre-wash of the alkaline water–oil emulsion, the aqueous phase was acidified and divided into three 100-ml portions and further extracted with 3 ml of diethyl ether, benzene and butyl acetate, respectively. The chromatograms of the extracts differ greatly in complexity. When diethyl ether was used, eight baseline-resolved peaks were recorded (Fig. 1d, sample I). Two peaks were identified by their retention times as 2-nitrophenol and 2,3-dinitrophenol. The same pattern was obtained for two waste samples analysed, here labelled I and II. The benzene extracts are significantly more complex, and those of butyl acetate exhibit only a 4–5-fold reduction in the number of peaks in comparison with the chromatogram of the new oil phase. With such a large number of peaks, one has to be careful with the assignment. Here, only those peaks coinciding within ± 0.03 min (2 s) with the retention time of the standard were identified as the corresponding phenols. The value of 0.03 min was selected as it had been found that this value approximated to the daily instrumental drift of the retention times of standard phenols.

Table I presents the results of the analysis of two waste water–oil liquids. Unrealistically high phenol concentrations when benzene or butyl acetate was selected as

the extractant indicate poor integrator peak assignment, a result of the complexity of the extract. The 4-amino antipyrine spectrophotometric method resulted in total phenol content of 0.42 and 0.64 mg/l for samples I and II, respectively, which agree well with the results of the GC analysis of the diethyl ether extracts. A similar agreement between the spectrophotometric and GC results was reported by Folke and Lund[6] for the analysis of phenols in municipal waste waters. The higher GC values can be ascribed to incomplete steam distillation of nitrophenols[3].

CONCLUSION

This work was partly aimed at studying the use of benzene and butyl acetate as extractants for phenols in acidic water media. The choice was made on the basis of literature information[7–9] on these two extractants, which are far superior to *n*-hexane and diethyl ether. Our experiments indicate that the benzene extraction of standard phenols from neutral water exhibits a low concentration factor, in accordance with the reported lower distribution coefficient for phenols[7–10]. To gain a desired concentration of phenols in the organic phase and to improve the GC detection limit, a benzene : water phase ratio exceeding 1 : 30 is used, and this has the drawback of a reduced extraction efficiency[6]. Butyl acetate, with distribution coefficients for phenols two orders of magnitude greater than those with benzene[7–10], completely extracts phenols in a single step, and the pre-concentration is easily carried out. Hence, butyl acetate is recommended for the extraction of trace amounts of phenols from organic samples. Unfortunately, butyl acetate is also a strong, non-selective extractant for non-phenolic species, so that in a system with hundreds of unknown components, it is almost impossible to resolve phenols from the maxtrix using GC analysis alone.

The extraction of phenols from a water–oil phase having a pH lower than 6 with diethyl ether is suitable for the determination of phenols in complex organic mixtures. The confident determination of phenols in crude waste oils is a future concern on which we hope to report soon.

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