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Note

Liquid chromatographic determination of traces of phenols in air

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Traces of phenols may be present in the atmosphere owing to automobile emission and photochemical production. Such phenols have often been sampled in an alkaline solution by using a fritted bubbler followed by liquid chromatographic (LC) analysis[1,2]. Recently, an LC technique for introducing a large volume of sample was developed for the determination of ultra-trace levels of phenols in environmental water[3]. However, considerable difficulty is encountered in storing and analyzing the samples at extremely low concentration levels because of their reactivity and adsorption on solid surfaces. Moreover, the complex sampling apparatus may be unsuitable in field research where a number of air samples should be sampled.

Several convenient methods have been developed for the determination of aldehydes[4], amines[5,6] and alkanethiols[7] in air samples by using Sep-Pak C_{18} (SP-18) sampling cartridges. In this paper, a convenient method is presented for the determination of ultra-trace levels of phenols in air. The phenols are sampled by the use of an SP-18 cartridge impregnated with sodium hydroxide and derivatized with *p*-nitrobenzenediazonium tetrafluoroborate (NBDATFB). The derivatives are introduced into a liquid chromatograph on a large scale through an ODS mini-column sampling loop. The method may be useful for determining parts per billion (ppb) or parts per trillion (ppt) levels of phenols such as those found in ambient air or industrial emissions in field research.

EXPERIMENTAL

Reagents and materials

All the reagents were of special grade and methanol was of chromatographic grade from Wako (Osaka, Japan). *p*-Nitrobenzenediazonium tetrafluoroborate (NBDATFB) was synthesized by the standard method[8].

Standard solutions were prepared to contain 1 mg/ml of phenol, *o*-cresol, *m*-cresol and *p*-cresol in methanol. NBDATFB solution was prepared by dissolving 0.1 g of NBDATFB in 100 ml of distilled water. The buffer solution (pH 11.5) was 0.51% sodium hydrogencarbonate–0.21% sodium carbonate in distilled water. The Sep-Pak C_{18} (SP-18) cartridge was obtained from Waters Assoc. (Milford, MA, U.S.A.).

Apparatus

A Waters Assoc. ALC/GPC 244 liquid chromatograph was employed,

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equipped with a mini-column sampling loop system and an M440 UV absorbance detector adjusted to 365 nm. The mini-column, attached to a Rheodyne (Cotati, CA, U.S.A.) 7125 six-way switching valve, was a 10.0 mm × 4.0 mm I.D. stainless-steel tube packed with 15–30-μm ODS silica (Nomura Kagaku, Aichi, Japan). The loop was washed with 5 ml of methanol prior to use. The analytical column was a 15 cm × 4 mm I.D. tube packed with Develosil ODS-3 (3 μm) (Nomura Kagaku). The mobile phase was methanol–water (85:15) and the flow-rate was 1.0 ml/min.

Preparation of sampling cartridge

The SP-18 cartridges were washed with 2 ml of methanol prior to use. A 2-ml volume of 0.1% sodium hydroxide in methanol was forced through the cartridge. The cartridge was dried for 1 h under reduced pressure in a nitrogen stream and then dried further by passing nitrogen (99.999%) at 70–100 ml/min for 30 min. The cartridge was closed with glass plugs, sealed in a vial and stored in a cool place in the dark until use.

Analytical procedure

A 2–100-l volume of air sample was sampled at 0.2–1.0 l/min through a coated SP-18 cartridge. The absorbed substances in the cartridge were eluted with 2 ml of methanol in the opposite direction to that used in sampling. The eluate was adjusted to pH 11.5 with the buffer, mixed with 0.5 ml of 0.1% sodium hydroxide solution and 0.5 ml of the NBDATFB solution, and then the volume was adjusted to 7 ml with water. A 0.1–3.0-ml aliquot of the sample was injected into the mini-column sampling loop. The adsorbed substances were introduced into the liquid chromatograph with the carrier in the opposite direction to that used in the injection and determined by LC. Identifications were made from the capacity factors (k') and quantitation was performed by measuring peak heights. The cartridges used could be used repeatedly at least five times by washing them with 3–5 ml of methanol each time.

RESULTS AND DISCUSSION

Adsorption and desorption of the phenols on and from the cartridge

A 200-l volume of an air sample containing 0.2–10.0 μg of the phenols, generated by using a Yuasa (Osaka, Japan) KS-04C standard gas generation apparatus (see Fig. 1), was passed at 1.5 l/min through two coated SP-18 cartridges in series. The phenols were detected on the first cartridge only and no phenols were found on the second. The adsorbed substances were completely eluted with 1.0 ml of methanol. As a result, the sampling volume of air and the elution volume of methanol were set to 100 l and 2.0 ml, respectively, in an usual determination.

Derivatization of phenols with NBDATFB in the methanol–water medium

Phenols couple with NBDATFB to form the red nitrobenzeneazo (NBA) derivatives in a weakly alkaline solution[1,2]. The reaction normally occurs at the *para* position in the phenols, but if the *para* position is blocked the reaction occurs at the *ortho* position. In the methanol–water reaction medium, the absorbance of the NBA

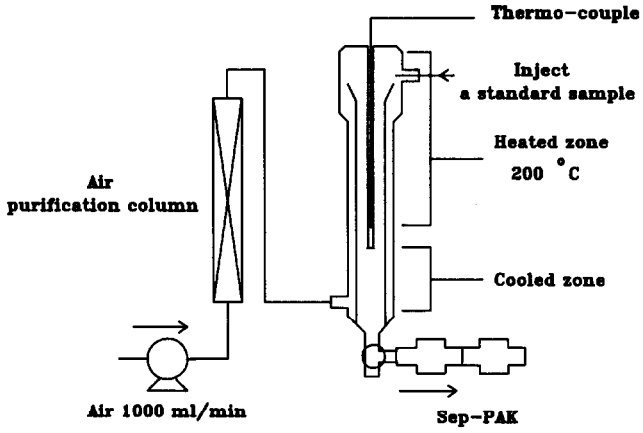

Fig. 1. Generation apparatus for standard phenol vapour.

derivatives reached a maximum very soon after the reaction began. The reaction seemed to be completed almost instantaneously, unlike that in aqueous media reported previously[1,2].

Sample introduction by the mini-column loop system

The reversed-phase mini-column (10 mm × 4 mm I.D. column packed with 15–30-μm ODS silica) was used to concentrate the NBA derivatives and to introduce them on a large scale into the liquid chromatograph to compensate for the insufficient response of the detector in trace analysis. In general, the retention volumes of the solutes are inversely proportional to the logarithm of the polarity of the eluent in a reversed-phase system. On this basis, the phenol-NBA derivatives that eluted first among the various derivatives were investigated with respect to the breakthrough

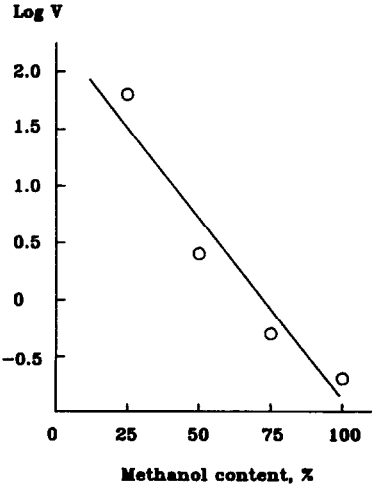

Fig. 2. Retention volume (V) of phenol-NBA derivative *vs.* percentage of methanol in methanol–water eluent.

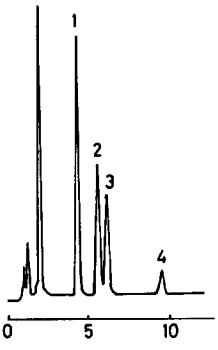

Fig. 3. Liquid chromatogram of NBA derivatives: (1) phenol, 10 ng; (2) *m*-cresol, 10 ng; (3) *o*-cresol, 10 ng; (4) *p*-cresol, 10 ng. Sample volume introduced, 3 ml; analytical column, 15 cm × 4 mm I.D., Develosil ODS-3; mobile phase, methanol–water (85:15) at 1.0 ml/min; UV detector, 365 nm.

behaviour on the mini-column by changing the methanol content in the methanol–water eluent. Fig. 2 shows the retention volumes of the derivatives *vs.* the percentage of methanol in the eluents. The percentage of methanol in the final sample was adjusted to 28–30% so as to make the breakthrough volume larger and to minimize the effects of water on the analytical column. The retention volume of the derivative could be more than 30 ml under the conditions used. However, the maximum volume of sample introduced was 3 ml in order to suppress background effects, which increased with increasing sampling volume. In calibration, excellent linearity was obtained for the phenols in the range 0.008–5.0 μg in 0.1–3.0 ml of sample introduced. Fig. 3 shows a typical chromatogram for the NBA derivatives with mini-column introduction. The minimum detectable amounts of the phenols were 0.2–2 ng.

Analytical accuracy and detection limits of phenol vapour

To investigate the analytical accuracy for phenol vapour, air samples containing 0.2–5.0 μg of the phenols were generated using the standard vapour generation apparatus. A 100-l volume of the air sample was sampled with a coated SP-18 cartridge and analysed for the individual phenols. Table I indicates that the recovery of

TABLE I

RECOVERY OF PHENOL VAPOUR IN AIR SAMPLES

*Phenol vaporized** (μg)*	*Average recovery ± S.D. (%)***			
	Phenol	*m-Cresol*	*o-Cresol*	*p-Cresol*
0.5	99.4 ± 1.4	98.4 ± 4.2	110.1 ± 2.7	103.4 ± 7.1
2.0	97.9 ± 1.3	99.2 ± 1.5	97.7 ± 4.5	90.5 ± 4.7
5.0	103.4 ± 1.6	98.0 ± 3.5	104.3 ± 2.1	100.0 ± 2.7

* Phenols were vaporized at 200°C and introduced into 1.0 l/min of air stream.

** Average of six runs.

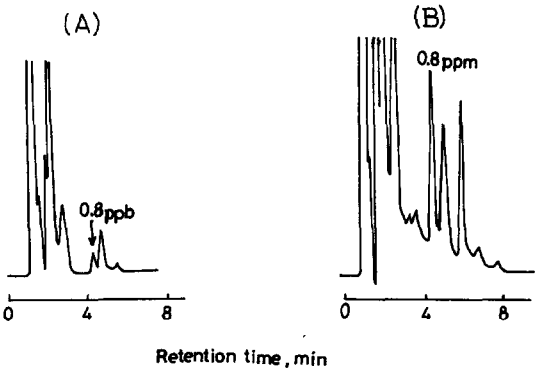

Fig. 4. Phenol in environmental samples: (A) atmosphere; (B) ambient air around an emission source. Analytical conditions as in Fig. 3.

the phenol vapors was 90.5–110.1% with a standard deviation of 1.3–7.1%. The detection limits of the phenol vapour were 0.2–0.3 ppt (v/v) for a 100-l air sample.

Stability of the sample

Phenols placed on the cartridge were recovered without loss after the cartridge had been stored for more than 2 weeks in a cool place (3–5°C) in the dark. The NBA derivatives were also stable for at least 2 weeks in the sample solution.

Application

The method was applied to the determination of phenols in atmospheric samples and in ambient air around an emission source. Fig. 4 shows typical chromatograms of phenol in environmental samples. Low ppb levels of phenol were easily determined without any effects of coexisting substances.

CONCLUSION

The proposed method may be useful for the determination of trace levels of phenols in ambient air, especially in field research. This technique will probably be applicable to many other types of sample after appropriate modification.

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