

## Note

### Headspace analysis of polar compounds in air

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Gaseous effluents in the detergent industry contain volatile organic substances such as C<sub>1</sub>–C<sub>4</sub> aliphatic alcohols, ketones and ethers, the approximate safety level of which in the atmosphere is 0.1 mg m<sup>-3</sup>. Although some gas chromatographic (GC) methods have been developed for the determination of atmospheric impurities, they are not applicable to polar organic impurities present in small concentrations without preconcentration.

To determine toxic organic compounds (C<sub>1</sub>–C<sub>3</sub> alcohols, acetone, methyl ethyl ketone and methyl isobutyl ketone), a method was developed previously for their headspace GC analysis with preliminary preconcentration in C<sub>4</sub>–C<sub>5</sub> alcohols<sup>1</sup>. However, we experienced serious interference problems with impurities in the absorbent.

We have now developed a procedure combining headspace analysis with preconcentration in water and salting out from sodium chloride solution and applied it to atmospheric measurements of *n*-butanol, isobutanol, ethyl acetate and butyl acetate. The preconcentration of polar compounds in water is preferable for their analysis. In this instance the purity of the absorbent can easily be ensured and further preconcentration of an extracted impurity is possible by the salting-out procedure.

The solubilities of the compounds of interest in water are: *n*-butanol 9.0 (15°C), isobutanol 9.5 (18°C), ethyl acetate 7.66 (15°C) and butyl acetate 0.5% (w/w) (25°C)<sup>2</sup>. The enthalpies of evaporation of *n*-butanol and ethyl acetate are: 52.30 and 32.26 kJ mol<sup>-1</sup>, respectively<sup>2</sup>.

The distribution coefficient (*K*) of an organic compound between water and air is the ratio of its concentrations in water (*C<sub>w</sub>*, mg l<sup>-1</sup>) and air (*C<sub>a</sub>*, mg m<sup>-3</sup>),  $K = C_w/C_a$ . The volatility behaviour (*F*) of an absorbent obeys the condition<sup>3</sup>  $FK < 0.5$ , where  $F = PM(RT\rho)^{-1}$ , *P* = vapour pressure, *M* = molar mass,  $\rho$  = density of absorbent, *R* = gas constant and *T* = absolute temperature.

Here we report a method for the extraction of atmospheric impurities from water for the GC determination of polar compounds in an air matrix at environmental levels.

## EXPERIMENTAL

All reagents were of analytical-reagent grade. For the preconcentration procedure we used an absorption vessel fitted with a porous glass plate and containing 4 cm<sup>3</sup> of distilled water. A gas stream at a flow-rate of 400 cm<sup>3</sup> min<sup>-1</sup> was introduced into the water through the porous plate.

The breakthrough volume of the gas to be analysed (air or standard mixture) is *ca.* 12 l. When equilibrium had been attained, a 1-cm<sup>3</sup> aliquot of solution was placed in a flask (*ca.* 15 cm<sup>3</sup>) for gas extraction. Tubes served to extract the volatile organic compounds from the water samples into air. The gas extraction tube had previously been filled with 1 cm<sup>3</sup> of water (for butyl acetate) or a mixture of 1 cm<sup>3</sup> of water and 0.5 g of sodium chloride (for *n*- and isobutanol and ethyl acetate). Both tubes were sealed with rubber corks, fixed in metallic chucks and shaken for about 15 min. The resulting vapour phase (1 cm<sup>3</sup>) was removed for GC analysis.

The measurements were carried with a Chrom-5 gas chromatograph equipped with a flame ionization detector and a glass column (1 m × 4 mm I.D.) of 15% polyethylene glycol 600 on Chezasorb AW. At flow-rates of the carrier gas (argon) of 25, hydrogen of 30 and air of 300 cm<sup>3</sup> min<sup>-1</sup> and an oven temperature of 130°C, the retention times of *n*-butanol, isobutanol, ethyl acetate and butyl acetate were 7.0, 3.0, 1.5 and 4.0 min, respectively.

Standard gas mixtures were prepared by a stepwise procedure. A known volume of liquid alcohol or ester was placed in a calibrated capillary thermostat tube (1.15 mm I.D.). Nitrogen was used as a gas diluent, as the diffusion coefficients of organic compounds in air and nitrogen are similar. Stable concentrations of gaseous alcohols and esters may be generated at the 0.08–1.0 mg m<sup>-3</sup> level by passing nitrogen over the surface in the capillary tube. The level of surface (and the amount of liquid evaporated) were determined to a precision of ±0.001 mm.

## RESULTS AND DISCUSSION

A typical chromatogram of the vapour phase is given in Fig. 1. The calibration graphs are linear in the ranges 0.02–0.24 mg cm<sup>-3</sup> for *n*- and isobutanol and butyl acetate and 0.01–0.3 mg cm<sup>-3</sup> for ethyl acetate.

We established the distribution behaviour of the alcohols and esters in the nitrogen–water system and examined the temperature dependence (Table I). The distribution behaviour of organic compounds obeys the equation

$$\ln K = \Delta H^\circ/RT + \Delta S^\circ/R$$

where  $\Delta H^\circ$  and  $\Delta S^\circ$  are the standard enthalpy and entropy of extraction, respectively. The linear dependence between  $\log K$  and  $1/T$  allows the  $K$  values to be determined if the absorption temperature differs from the examined values (Table I). For comparison, the distribution coefficients in the nitrogen–*n*-butanol system are 1050, 5630 and 6770 for methanol, ethanol and *n*-propanol, respectively, and in the nitrogen–*n*-amylalcohol system they are 307, 580 and 1035 for acetone, methyl ethyl ketone and methyl isobutyl ketone, respectively.

The sampling temperature is limited by freezing of the absorbent in the porous

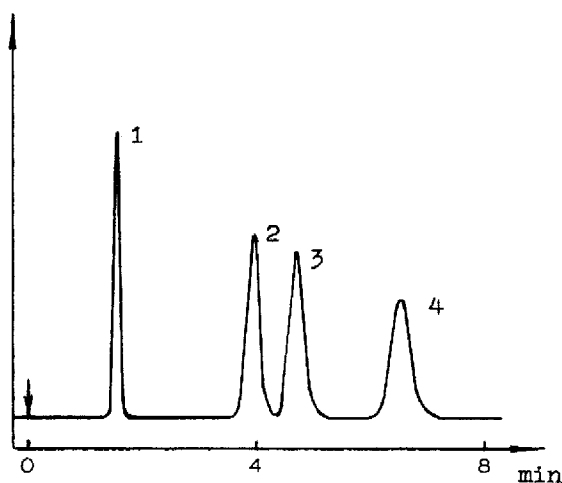


Fig. 1. Typical chromatogram of the vapour phase: 1 = ethyl acetate; 2 = isobutanol; 3 = butyl acetate; 4 = *n*-butanol.

TABLE I

DISTRIBUTION COEFFICIENTS IN THE NITROGEN-WATER SYSTEM

Temperature (°C)	K			
	<i>n</i> -Butanol	Isobutanol	Ethyl acetate	Butyl acetate
10	6250 ± 35	3238 ± 25	1125 ± 10	1660 ± 20
20	1220 ± 22	1038 ± 15	572 ± 8	1480 ± 11
25	897 ± 5	599 ± 6	450 ± 5	1080 ± 12
35	252 ± 10	205 ± 15	180 ± 7	814 ± 20
45	—	—	—	577 ± 18

plate and by the increase in gas solubility at low temperature. The range of measured concentrations depends on the absorption temperature (Table II).

The detection limits are 1.0, 5.0, 0.3 and 0.35 mg m<sup>-3</sup> for methanol, ethanol, *n*- and isobutanol and ketones, respectively.

TABLE II

RANGE OF MEASURED CONCENTRATIONS OF ALCOHOLS AND ESTERS

Temperature (°C)	C <sub>a</sub> (mg m <sup>-3</sup> )			
	<i>n</i> -Butanol	Isobutanol	Ethyl acetate	Butyl acetate
10	0.08–1.2	0.07–1.1	0.08–1.2	0.08–1.2
20	0.41–6.1	0.23–3.5	0.16–2.4	0.09–1.3
25	0.56–8.4	0.40–6.0	0.20–3.0	0.12–1.8
35	2.0–30	1.2–17.6	0.47–7.1	0.16–2.4

According to the concentration level expected, the sampling temperature can be determined. The detection limit depends on the absorption temperature. The analytical precision at 10°C is 7.0% for *n*- and isobutanol, 14.5% for ethyl acetate and 9.6% for butyl acetate.

#### REFERENCES

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