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MASS SPECTROMETRIC IDENTIFICATION OF 2-ETHYLHEXANOL IN INDOOR AIR: RECOVERY STUDIES BY CHARCOAL SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS AT THE MICROGRAMS PER CUBIC METRE LEVEL

BARBRO ANDERSSON*, KURT ANDERSSON and CARL-AXEL NILSSON
National Board of Occupational Safety and Health, Department of Occupational Health in Umeå, Box 6104, S-900 06 Umeå (Sweden)
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SUMMARY

2-Ethylhexanol was identified in office indoor air by combined gas chromatography–mass spectrometry and a method for charcoal sampling and gas chromatographic analysis at the $\mu g/m^3$ level was evaluated. The influence of relative humidity (20 and 85%) and storage time (4 weeks) was tested and found to be insignificant. The overall detection limit is 10 $\mu g/m^3$.

INTRODUCTION

Reports of impure indoor air and its effects on health have increased during the past two decades. Many volatile organic compounds have been identified in indoor air samples[1–5] and are considered to be the main causes of these problems. The pollutants arise from man and his activities, from various building materials[6] and from outdoor sources[7]. More than 100 organic compounds can be identified in the indoor air of newly built houses[7]. Although they occur in very low concentrations, usually at the $\mu g/m^3$ level, some of these compounds have noticeable effects on man, such as nose, throat and eye irritations, unnatural tiredness and headaches (the "sick-building syndrome"). One of these compounds is the volatile alcohol 2-ethylhexanol[7], which has a low odour level. In animal experiments, 2-ethylhexanol was reported to act as an eye irritant and to affect the nervous system and lung function[8–10].

In the literature, methods evaluated for the analysis of 2-ethylhexanol in air are limited to a recent report by Russo and Hee[11]. Their method was designed for personal sampling of 2-ethylhexanol, present in high concentrations (110–650 mg/m^3; 20–120 ppm), in the air in industrial environments. Sampling was performed on Chromosorb 102 and the gas chromatographic (GC) analysis was carried out on a packed column with flame-ionization detection.

In this paper, the identification of 2-ethylhexanol in the office environment is reported. Sampling on charcoal at various relative humidities, sample storage stability and a capillary GC analysis were evaluated at the $\mu g/m^3$ level of 2-ethylhexanol in air.

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EXPERIMENTAL

Reagents

Charcoal tubes (coconut-base, glass tubes with two sections, 100 + 50 mg; SKC Inc., lot 120), 2-ethylhexanol (98%; Merck-Schuchardt), acetone, carbon disulphide and dichloromethane (all analytical-reagent grade; Merck) and diethyl ether (analytical-reagent grade; Mallinckrodt) were used.

Test system

In our laboratory, a system producing air with a known flow-rate and relative humidity is used in recovery tests[12]. After passage through a dust/oil filter, pressurized air is humidified in gas bottles and diluted with unsaturated air in chambers. The flow is then divided into seven equal parts, passing through six parallel charcoal tubes (one being used as a blank) and an air humidity indicator. This system enables small adjustments to be made to both flow-rate and humidity. Sampling was performed at 20 and 85% relative humidity (RH) and with an air flow-rate of 200 ml/min.

Gas chromatography

GC was carried out on a Hewlett-Packard Model 5880A gas chromatograph with a microprocessor and a flame-ionization detector. The chromatograph was equipped with an automatic liquid sampler (Hewlett-Packard Model 7671A) and a 50 m × 0.20 mm I.D. OV-101 fused-silica column (Hewlett-Packard). The injector and detector temperatures were 200 and 250°C, respectively. Nitrogen was used as the carrier gas, at a column flow-rate of 1 ml/min. When the sample was injected in the split mode (2 μl, splitting ratio 1:30) the analysis was performed isothermally at an oven temperature of 130°C (retention time 7 min). For the lowest concentrations of 2-ethylhexanol, 2-μl samples were injected in the Grob splitless injection mode (45 sec). The column temperature was 40°C for 5 min, and was subsequently increased at 10°C/min to 200°C, which was held for 10 min (retention time 15 min). A subsequent temperature increase to 220°C was held for 10 min (column conditioning). The split flow was 20 ml/min and the septum flush 10 ml/min.

Gas chromatography–mass spectrometry (GC–MS)

The gas chromatograph was connected to a Finnigan Model 4021 mass spectrometer via a heated copper line, through which the capillary column passed through the separator oven into the ion source. Helium was used as the carrier gas and the other GC parameters were as above. The temperature of the copper line was held at 180°C and that of the mass spectrometer separator oven and ion source at 250°C. Spectra were recorded at 70 eV, with an electron multiplier voltage of 1600 V and a pre-amplifier setting of 10^{-7}.

Recovery study

The recovery studies were carried out at four different concentrations of 2-ethylhexanol in air, *viz.*, 10, 1, 0.1 and 0.01 mg/m^3. Samples of 10 μl of 2-ethylhexanol in dichloromethane (concentrations 10.0, 1.0, 0.10 and 0.050 μg/μl) were applied to five parallel charcoal tubes via 10-cm glass tubes equipped with glass-wool plugs at

each end. The temperature was 22°C and the pumped air volumes were 10, 10, 10 and 50 l, which correspond to the air concentrations above. Finally, the charcoal was carefully agitated for 30 min with 1.0 ml of dichloromethane in 3.5-ml glass vials with screw-caps (Ika Vibrax-VXR vibrator) before the GC analysis.

Storage tests were performed at 6 and at 22°C with the charcoal tubes wrapped in aluminium foil. The concentration of 2-ethylhexanol corresponded to 0.10 mg/m^3 and the storage time was 4 weeks.

Field study

Charcoal samples (30–60 l air volume) from an office work-room environment were treated as above and analysed by GC and GC–MS within 5 days. For sampling, an SKC Model 222-3 pump with an air flow-rate of 200 ml/min was used.

RESULTS AND DISCUSSION

In office indoor air, the concentrations of organics with expected physiological activity are usually about 1/1000–1/100th of the Swedish threshold limit values. Accordingly, greater demands are placed on both sampling and analysis compared with methods designed for the industrial work-room environment. The following points are put forward for consideration in planning an investigation of organics in office indoor air at the μg/m^3 level.

Choice of sorbent. If possible, the sorbent should allow the sampling of a wide range of organics and provide a low background contribution in the analysis. Charcoal has the advantage of complying with both of these requirements and also of maintaining a high sample capacity at high air humidity. Porous polymers are reported to give an interfering background at this low-level analysis and to require extensive cleanup before sampling[13,14].

Desorbent. The polarity of the organics sampled and the solvent must be considered so as to obtain a satisfactory recovery. If GC analyses are used, the solvent should be suitable for splitless or on-column injection techniques and be of sufficient purity with regard to the analytical background.

Sampling time and sampling volume. The volumes of the air samples are partly determined by the detector sensitivity in the final analysis. When personal sampling is required, the sampling time should be such that sampling is finished within a working day.

Selectivity. As there are many organics in indoor air at the μg/m^3 level, the samples must be analysed with sufficient sensitivity. In GC analysis, packed columns are preferably replaced with capillary columns. Identification, however, often requires combined capillary GC–MS.

Repeated analysis. Repeated analysis of the same sample is necessary for high precision in the quantitative analysis and for confirmation of the identity of the organics in the sample.

To meet the above requirements, the method for sampling and analysis of 2-ethylhexanol was designed as follows. No threshold limit value for 2-ethylhexanol has been established in Sweden but 10 μg/m^3 of 2-ethylhexanol in air was decided as the minimum for a practical detection limit. GC with a capillary column and flame-ionization detection was chosen to combine good sensitivity with high reso-

lution, thus permitting the separation of 2-ethylhexanol from other compounds in the sample. To make the method suitable for personal sampling, a sampling flow-rate of 200 ml/min was chosen, which, owing to the GC sensitivity, results in a sampling time of less than 4.5 h.

As activated charcoal has been demonstrated to be useful for the sampling of a large number of organics in air and as it fulfils the requirement of giving a low blank, the recovery from this sorbent was evaluated. 2-Ethylhexanol levels in air ranging from 10 to 10,000 $\mu g/m^3$ and air relative humidities of 20 and 85% were chosen and various solvents for desorption were evaluated (Table I).

Carbon disulphide and diethyl ether are usually used for desorbing organics from charcoal but resulted in lower recoveries than dichloromethane: 72 and 81%, respectively (1 mg/m^3 of 2-ethylhexanol, 20% RH). In order to increase the polar character of the solvent, 5% acetone in dichloromethane was tested and resulted in the same recovery as pure dichloromethane at 20% RH. However, at 85% RH the recovery was 10% lower, which cannot be explained at present.

Dichloromethane, affording the highest recovery, is also suitable for Grob splitless injection and is available in sufficiently pure quality. Thus, it combines all the desired requirements for a suitable solvent. Solvent desorption also provides the possibility of repeated analysis and identification.

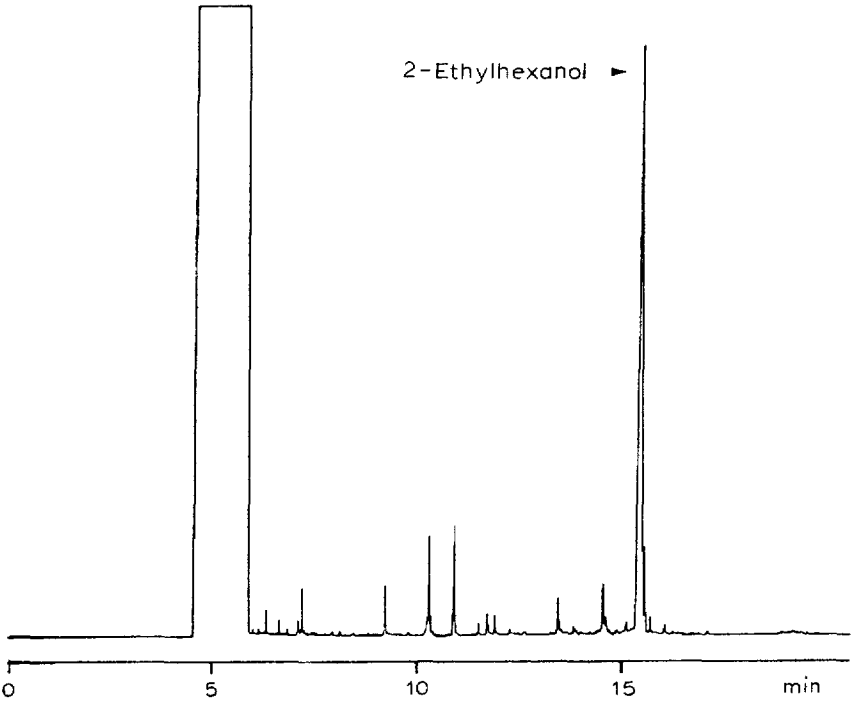

Fig. 1. Gas chromatogram showing indoor air pollution by 2-ethylhexanol in a governmental office building. Dichloromethane used as desorbent, OV-101 fused-silica column and Grob splitless injection.

TABLE I

RECOVERY OF 2-ETHYLHEXANOL FROM ACTIVATED CHARCOAL AT DIFFERENT AIR LEVELS AND RELATIVE HUMIDITIES (RH)

Dichloromethane was used for desorption and the recoveries are calculated as means of five replicates with relative standard deviations (R.S.D.) (coefficients of variation).

2-Ethylhexanol concentration in air (mg/m³)	*Sample volume (l)*	*20% RH*		*85% RH*	
		Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*
0.010	50	96	3	96	3
0.10	10	97	4	96	4
1.0	10	97	3	97	3
10	10	97	3	96	2

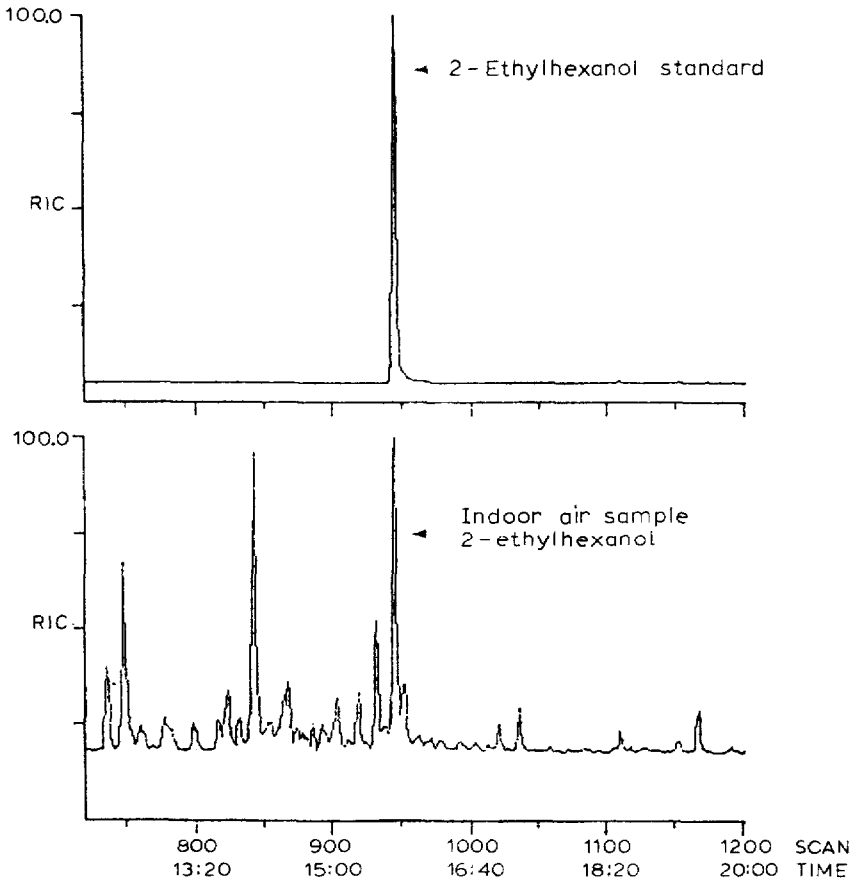

Fig. 2. Reconstructed ion chromatogram of 25 ng of 2-ethylhexanol standard compared with an indoor air sample (80 $\mu g/m^3$ of 2-ethylhexanol). Dichloromethane used as desorbent, OV-101 fused-silica column and Grob splitless injection.

TABLE II

INFLUENCE OF STORAGE ON RECOVERY OF 2-ETHYLHEXANOL FROM ACTIVATED CHARCOAL

Dichloromethane was used for desorption and recoveries are calculated as means of five replicates with relative standard deviations (R.S.D.) (coefficients of variation). Storage time, 4 weeks; air level, 0.10 mg/m^3; sample volume, 10 l.

Storage temperature (°C)	*20% RH*		*85% RH*	
	Recovery (%)	*R.S.D. (%)*	*Recovery (%)*	*R.S.D. (%)*
10	95	4	96	4
22	95	6	96	6

To ensure that the method meets the requirement of sample stability, samples of 2-ethylhexanol were stored for 4 weeks at room temperature and in a refrigerator. Sampling was performed at 20 and 85% RH. The results (Table II) indicate that storage did not affect recovery.

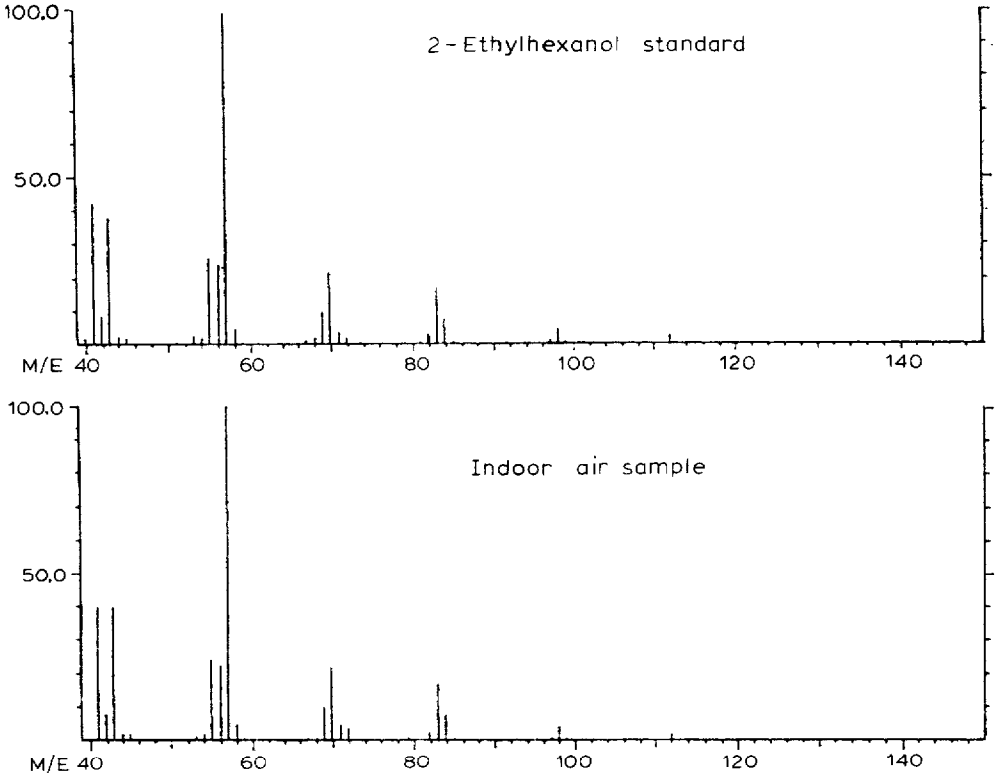

Fig. 3. Mass spectra of 25 ng of 2-ethylhexanol and the corresponding sample peak in Fig. 2 (M^+ = 130).

The method was used in a study of indoor air in a governmental office building. The study was initiated following complaints about irritation caused by the indoor air and the occurrence of diverse symptoms as described in the Introduction. Samples were taken as imission samples in different rooms. Fig. 1 shows a typical gas chromatogram from a room with relatively high levels of 2-ethylhexanol (1 mg/m^3). Other components in the chromatogram are terpenes from the woodwork and common solvents from paint, etc. Fig. 2 shows a reconstructed ion chromatogram from a mass spectrometric analysis of a sample from another room with a considerably lower level of 2-ethylhexanol. It is evident that at this low level the resolving power of a capillary column is needed for adequate analysis. The level of 2-ethylhexanol in this sample is about 10 μg/m^3. Fig. 3 shows the mass spectra of 2-ethylhexanol and the compound giving rise to the peak in Fig. 2 with the same retention time as 2-ethylhexanol. As can be seen, the resemblance is good.

Phthalate esters, mostly bis(2-ethylhexyl) phthalate (dioctyl phthalate), are considered to be the origin of 2-ethylhexanol. These substances are used as plasticizers in floor coverings. A damp environment and a high pH value, caused by the concrete, are considered to result in hydrolysis of the dioctyl phthalate[15]. Ammonia from microdegradation of casein in damp self-levelling screed has also been discussed as a possible reason for the hydrolysis. At present, it is not clear how 2-ethylhexanol is formed.

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