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Journal of Chromatography A, 668 (1994) 371–374

JOURNAL OF
CHROMATOGRAPHY A

Preconcentration and determination of 2,4,5-trichlorophenol in air using a wet effluent denuder and high-performance liquid chromatography

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Abstract

A wet effluent diffusion denuder was used for the preconcentration of gaseous 2,4,5-trichlorophenol (2,4,5-TCP) from air. The wet denuder function is based on capturing gaseous pollutants from air in a film of absorbing liquid that flows continuously down the inner wall of the wet denuder. The air passes through the cylindrical wet denuder under laminar flow conditions. Water (adjusted to pH 8.5) was employed as absorbing liquid. The concentration of 2,4,5-TCP was determined using a liquid picochromatography with a reversed-phase C_{18} stationary phase and UV detection at 218 nm. The detection limit was 685 ng m^{-3}. The measuring systems enables results to be obtained at 7-min intervals.

1. Introduction

Hundreds of different organic substances are emitted into the air and many of them have adverse health effects at trace concentrations. The increasing interest in understanding the distribution and fate of organic compounds in the atmosphere initiated the development of more accurate, sensitive and reliable techniques for their monitoring. An important feature of the techniques is how fast results can be obtained (*i.e.*, the time elapsed between the sample collection and the end of analysis). Filter pack techniques have been widely applied for both gas-phase and gas/particle distribution studies [1–6]. These filter/sorbent systems suffer from artifacts caused by adsorption of gas-phase analytes on the filter or on the collected particles or, on the other hand, by volatilization of analytes from the particles [1,7]. These techniques are often time consuming.

In recent years, diffusion denuders have replaced the commonly used filter packs in some instances to prevent these difficulties. The diffusion denuder is a tube (cylindrical design) or several (usually two) concentric tubes (annular design) through which sample air passes. Under laminar flow conditions, particles pass through the denuder owing to their small diffusion coefficients and then they can be collected downstream of the denuder. Gas molecules diffuse towards the inner tube walls covered with an appropriate sorptive agent in which molecules are accumulated. After sampling, the analyte is usually removed from the surface of the denuder walls by thermal desorption or liquid extraction [8–16]. These procedures, especially liquid extraction, are accompanied by some problems, but the construction of a wet effluent diffusion denuder (wet denuder) [17,18] makes it possible

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0021-9673/94/$07.00
SSDI 0021-9673(93)E1130-R

to avoid them. Instead of the fixed film of sorptive agent, a film of absorbing liquid flows continuously down the inner wall of the wet denuder while gas passes countercurrently and, in this way, a continuous stream of concentrated analyte is obtained at the bottom of the denuder. The concentrate can be analysed directly or further treated. The concentration effect is given by the ratio between the liquid flow-rate (hundreds of μl/min) and the gas flow rate (l/min), with an assumed denuder collection efficiency of 100%.

The use of a wet denuder for the preconcentration of gaseous model organic compounds was verified in this work.

2. Experimental

2.1. Wet denuder

The wet denuder was a glass tube (50 cm × 1 cm I.D.), the inner wall of which had been treated by a special procedure [17,18] to maintain a compact film of absorbing liquid (water). The vertical position of the denuder ensured its correct operation. The liquid was fed to the denuder wall through a porous PTFE ring (Porex Technologies, Fairburn, GA, USA) located in the head at the upper end of the denuder. The concentrate was also removed through the head with a PTFE ring at the lower end of the denuder. The concentrate was sucked into a vial by a peristalic pump (laboratory made) and was taken from this vial for analysis. The sampled air entered the denuder through a subduction zone (glass tube, 15 cm × 1 cm I.D.) which ensured adjustment of laminar flow conditions. The air flowed through the denuder in the reverse direction to the absorbing liquid. A membrane pump (JZD, Výčapy, Czech Republic) was located downstream of the denuder.

2.2. HPLC system

A PLC-10 picochromatograph with a glass-fibre UV detection cell (laboratory made) was used [19]. A Jasco (Tokyo, Japan) 875-UV detector was connected to the detection cell and set at 218 nm. A glass column (60 mm × 0.5 mm I.D.) packed with Silasorb C_{18} (5 μm) (Lachema, Brno, Czech Republic) was used, with acetonitrile–water (65:35) as the mobile phase at a flow-rate of 7 μl min^{-1}. The sample volume was usually 10 μl. The principle of sample injection in a non-eluting solvent was applied (sample flow-rate 5 μl min^{-1}) [20].

2.3. Vapour generator

The condenser inside which the solid phase 2,4,5-trichlorophenol (2,4,5-TCP) (Merck, Darmstadt, Germany) was inserted worked as a source of gaseous 2,4,5-TCP at a temperature of 10°C. Nitrogen was passed continuously through the condenser at 0.5 ml min^{-1} and transported 2,4,5-TCP to a T-piece where it was mixed with air that has been cleaned through a charcoal trap. This gas mixture was led to the wet denuder. When dilution was necessary, the part of the nitrogen containing 2,4,5-TCP was withdrawn with a peristaltic pump (Laboratory Equipment, Prague, Czech Republic) before mixing with air. The production of the generator was measured by HPLC (see above) after 2,4,5-TCP had been collected in deionized water. To verify this method, GC with flame ionization detection (Carlo Erba, Milan, Italy; Hewlett-Packard SE-54 capillary column, 30 m × 0.53 mm I.D.; carrier gas nitrogen) was used for the determination of 2,4,5-TCP, after the 2,4,5-TCP had been absorbed in toluene (Lachema). The same volume of solvent (0.5 ml) was always used and the collection times were varied in the range 20–70 min. Both methods gave comparable results. Two collection vials were used in series for the first measurements. No 2,4,5-TCP was found in the second vial and therefore only one vial was used in further experiments. The production of the generator was always determined before denuder experiments.

3. Results and discussion

The simple model system was used to test the wet denuder. 2,4,5-TCP was chosen because of its relatively good solubility in water, which is why water could be used as the absorbing liquid. 2,4,5-TCP is employed in the manufacture of pesticides, dyes, etc., and is an air pollutant, especially in workplaces.

The length of the denuder was chosen as 50 cm so that the collection efficiency (c/c_0) was at least 99% for an air flow-rate of 0.5 l min^{-1}. It was calculated according to the Gormley and Kennedy equation [21,22], which describes the behaviour of trace amounts of gases in a cylindrical denuder:

$$
\begin{aligned}
c/c_0 = {} & 0.819\exp(-14.6272\Delta) \\
& + 0.0976\exp(-89.22\Delta) \\
& + 0.01896\exp(-212\Delta) \\
\Delta = {} & \pi DL/4F
\end{aligned}
$$

where c = mean concentration of the gas trace leaving the denuder, c_0 = concentration of the gas trace entering the denuder, D = diffusion coefficient of the gas trace, L = denuder length and F = gas flow-rate. If Δ is sufficiently low, only the first term of the equation is significant and the equation is simplified.

To verify the expected efficiency of the wet denuder we performed series of repeated experiments at a constant 2,4,5-TCP concentration. The air flow-rate was 0.5 l min^{-1} and the water flow-rate was varied from 100 to 350 μl min^{-1}. During the experiments we found that the liquid flow-rate had to be maintained above 250 μl min^{-1}. Below this flow-rate, the liquid film is probably not compact because the wet denuder wall is slightly rough (tens of μm) after treatment. Water was adjusted to pH 8.5 for better denuder operation. The use of water also restricts the influence of air humidity on denuder operation. Changes in relative humidity cause only various evaporative losses of water, which do not affect the collection procedure when the liquid flow-rate is sufficiently high [17].

Under these conditions, we obtained a collection efficiency of 100.6% with R.S.D. = 5.9% for seven samples taken during 5 h at a 2,4,5-TCP concentration of 21.4 μg m^{-3}. The calculated efficiency was 99.1% if the value of the diffusion coefficient was $6.54 \cdot 10^{-2}$ cm^2 s^{-1} (25°C). It was calculated according to the method of Fuller, Schettler and Giddings [23]. It should be noted there were more sources of errors (not only denuder operation) that contributed to total R.S.D. value, *e.g.*, fluctuation of nitrogen flow through the vapor generator (1.5%), error of LC determination (3.0%) and error of liquid flow-rate determination.

The relationship between collection efficiency and air flow-rate was measured in the range 0.4–1.8 l min^{-1} (Fig. 1). The shape of the curve corresponds to the curve calculated according to the Gormley and Kennedy equation. This confirms that water is a good absorption liquid under the given conditions.

The sets of data obtained in measurements of previous dependences were also used for calculation of the diffusion coefficient of 2,4,5-TCP. It is obvious that the diffusion coefficient can be determined from the slope of a plot of Δ *versus* L/F (Fig. 2). Values of the parameter Δ were calculated from the Gormley and Kennedy equation when known c and c_0 values were substituted. The average value of the diffusion coefficient of 2,4,5-TCP (from five measurements) was $6.13 \cdot 10^{-2}$ cm^2 s^{-1} with R.S.D. = 14.9%. In spite of the experiments performed without holding the air temperature constant (laboratory temperature was 26 ± 1°C), this diffusion coefficient was comparable to the theoretically calculated value of $6.67 \cdot 10^{-2}$ cm^2 s^{-1} at 26°C.

The calibration graph was measured in the

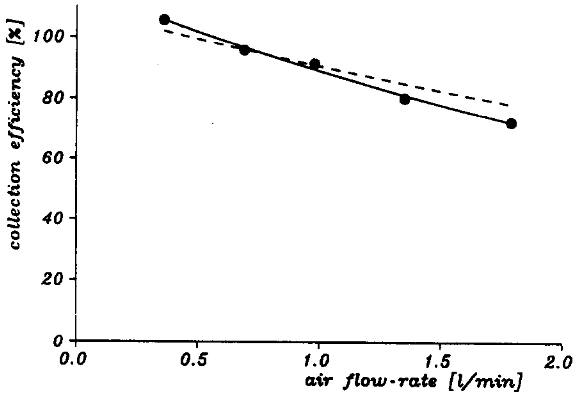

Fig. 1. Relationship between wet denuder collection efficiency and air flow-rate. ● = Experimental data; dashed line = theoretical curve according to the Gormley and Kennedy equation.

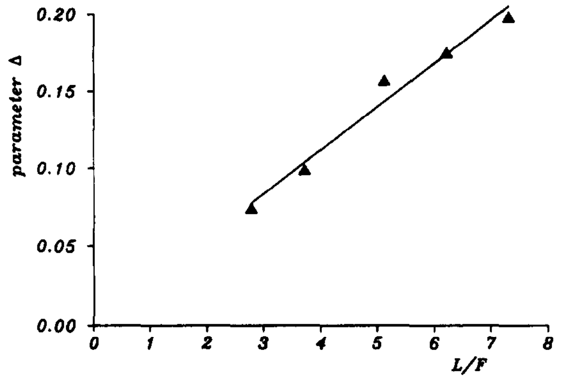

Fig. 2. Plot of parameter Δ *versus* L/F for calculating the diffusion coefficient of 2,4,5-TCP.

range of available concentrations 10–40 μg m^{-3}. The plot of peak area *versus* 2,4,5-TCP concentration was linear ($r = 0.998$) under the given conditions (250 μl min^{-1} liquid and 0.5 l min^{-1} air flow-rates). The estimated detection limit for injection of 10 μl of concentrate was 685 ng m^{-3} (calculated from three times the baseline noise). This limit could be lowered by increasing the sample volume.

The connection of the wet denuder with the picochromatograph allows a result to be obtained every 7 min.

4. Conclusions

The wet denuder proved successful for the collection of gaseous 2,4,5-TCP from air and it could be expected to be applicable also to other classes of organic pollutants if the appropriate absorbing liquid is chosen. The continuously renewed collection surface, the rapidly obtainable concentrate of analytes and the possibility of direct analysis of this concentrate are advantages of the wet denuder.

5. Acknowledgements

This work was supported by a grant (No. 63157) from the Academy of Sciences of the Czech Republic. The authors thank Dr. V. Kahle for technical assistance and for advice.

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