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Journal of Chromatography A, 918 (2001) 153–158

JOURNAL OF  
CHROMATOGRAPHY A

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# Wet effluent diffusion denuder technique and determination of volatile organic compounds in air

## I. Oxo compounds (alcohols and ketones)

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Received 5 December 2000; received in revised form 20 February 2001; accepted 2 March 2001

### Abstract

The wet effluent diffusion denuder (WEDD) preconcentration technique for the determination of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, acetone, methyl ethyl ketone, diethyl ketone and methyl *n*-propyl ketone in air is discussed. The compounds are continuously collected into a thin film of deionized water flowing down the inner wall of the cylindrical wet effluent diffusion denuder. The concentrate is analysed by gas chromatography. Detection limits of alcohols and ketones are as low as 1  $\mu\text{g/l}$  (GC–flame ionization detection) and/or 1  $\text{ng/l}$  (GC–MS). This technique could be applicable for the continuous monitoring of ppb (v/v) levels of both alcohols and ketones in the air. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Instrumentation; Diffusion denuder; Denuder; Sample handling; Air analysis; Alcohols; Ketones

### 1. Introduction

Scientific and public concern about the origin, transport and influences of organic and inorganic atmospheric pollutants on the biosphere have led to enrichment techniques becoming an integral part of air trace analyses [1,2]. Among “older” enrichment techniques, impinger absorption procedures, techniques based on adsorption on sorbents and/or cryofocusing, which are cut-down mostly due to the sub-ppb (v/v) concentrations of the compounds in question in the air and the stability of the determined compounds, denuder techniques are enjoying atten-

tion. However, inorganic trace gaseous pollutants are frequently preconcentrated in diffusion denuders and it has been proven that the reliability of results based on this preconcentration technique is excellent [3–5], the preconcentration of organic compounds based on the use of the denuders is not so frequent. For preconcentration of non-volatile and semi-volatile organic compounds the different shapes of so-called “dry” denuders have been used [5–7], including curious designs of annular denuder [6–9] and the diffusion denuder [10] made up of 120 parallel connected 25-cm long capillary columns (DB-1, I.D. 320  $\mu\text{m}$ ) for example. These preconcentration procedures have in common the fact that after preconcentration the organic compounds are heat desorbed, or extracted from the denuder with an appropriate solvent and analysed. The methodical

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disadvantage of these “dry” denuder preconcentration procedures is discontinuity.

The use of a concentrating apparatus with a moving film of absorption liquid, which makes possible the real-time analysis of organic analytes in air, is still only sporadic. A diffusion scrubber was part of the flow injection analysis (FIA) system, which made possible the determination of formaldehyde [11]. A cylindrical wet effluent diffusion denuder (WEDD) [12] has been used for continual preconcentration and the determination in air of polar 2,4,5-trichlorophenol, which was effectively collected into deionized water [13]. The less polar 1,4-dichlorobenzene was preconcentrated in 1-propanol [14].

Because application of the wet effluent diffusion denuder technique as a standard preconcentration procedure for trace air organic compounds requires more information, this paper describes the behaviour of the polar compounds: alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol) and ketones (acetone, ethyl methyl ketone, diethyl ketone and methyl *n*-propyl ketone) in an air–water system within the cylindrical WEDD.

## 2. Experimental

### 2.1. Equipment

The gas chromatographic measurements were carried out with a Chrom 5 Gas Chromatograph (Laboratory Equipment, Prague, Czech Republic) with a flame ionization detector, packed glass column (1.5 m×4 mm I.D.), stationary phase of 10% Carbowax 20M on Chromosorb W (80–100 mesh), nitrogen carrier gas and column temperature 60–140°C. A GC-8000 series gas chromatograph with “mass detector” MS Trio-1000 (Fisons Instruments), the capillary column 007-5MS (30 m×0.18 mm I.D.×0.25- $\mu$ m film, Quadrex) has also been available for experiments (helium, column temperature 40–200°C).

### 2.2. Standard gas mixtures

A continuous stream of standard mixtures of alcohols and ketones (analytical-reagent grade, La-

chema, Brno, Czech Republic) in nitrogen with defined contents of substances were prepared by the procedure outlined by Vejrosta and Novák [15]. Where an accurately controlled stream of nitrogen is forced at a low flow-rate through a thermostated glass saturator packed with Chromosorb P (60–80 mesh) impregnated approximately 30% (w/w) of the studied oxo compounds.

### 2.3. Wet effluent diffusion denuder

The wet effluent diffusion denuder [12] consisted of a treated glass tube (40 cm×1.1 cm I.D.×1.4 cm O.D) and untreated inlet and outlet tubes, assembled at two heads. The inlet tube (11 cm×1.1 cm I.D.) was used to adjust the laminar flow of sampled air into the WEDD. A denuder tube of length of 40 cm was chosen to attain satisfactory collection efficiency. The mounting heads and a tamping are made from inert materials (polycarbonate, PTFE, Viton O-ring).

### 2.4. Experimental procedure

A detailed illustration of the individual parts of the experimental apparatus is given in Fig. 1. A flow-rate of pure nitrogen from a cylinder flowing through the saturator (S), placed in a water thermostat (21±0.05°C), is measured by a differential manometer (DFM). The gas outlet of the saturator is connected by PTFE capillary to the inlet of the denuder, where the vapour of the studied substances was mixed with humidified air, prepared by passing dry air through a Nafion membrane tubing (NT) immersed in a water bath (TB). Deionized water (500  $\mu$ l/min) was fed (PP<sub>1</sub>) into the denuder tube through a porous PTFE O-ring located between the outlet tube and the wetted part of WEDD. A concentrate of analyte was aspirated through a second PTFE O-ring, placed between the bottom of the denuder tube and the inlet tube, with a peristaltic pump (PP<sub>2</sub>) and is taken for gas chromatographic analysis.

The behaviour of oxo compounds in the WEDD has been studied for air flow-rates 416–1217 ml/min and temperatures of 10, 20 or 30°C, respectively. The air was prepared by passing outdoor air through a charcoal trap (CHF<sub>2</sub>) and humidifier (NT) to a T-piece from where cleaned and humidified air was

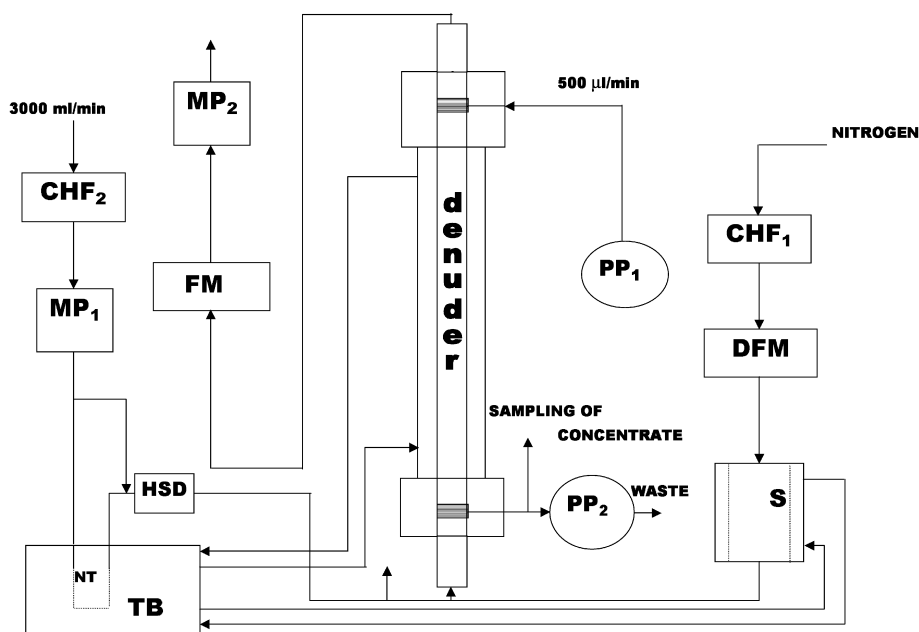


Fig. 1. The scheme of the measuring system. CHF<sub>1</sub>, CHF<sub>2</sub>, charcoal filters; DFM, differential manometer; S, saturator; PP<sub>1</sub>, PP<sub>2</sub>, water supplies and concentrate aspirates peristaltic pumps; MP<sub>1</sub>, MP<sub>2</sub>, membrane air pumps; TB, water bath with Nafion humidifier (NT); FM, air flow meter (rotameter); HSD, humidity sensor.

sucked into the WEDD by a membrane pump located downstream (MP<sub>2</sub>). The concentration of the studied alcohols and ketones in the air entering the denuder was kept constant within the above-mentioned flow-rates at 7.846 mg/l (methanol) 5.149 mg/l (ethanol), 2.219 mg/l (*n*-propanol), 0.079 mg/l (*n*-butanol), 0.035 mg/l (*n*-pentanol), 26.801 mg/l (acetone), 13.360 mg/l (methyl ethyl ketone), 6.048 mg/l (diethyl ketone) and 5.802 mg/l (methyl *n*-propyl ketone), respectively. These concentrations were controlled (FM) by the nitrogen flow-rate through the saturator in the range from 17 to 49.6 ml/min.

The analyte concentrate was analysed by GC–flame ionization detection (FID). The injection volumes were 5 µl of water and 1 ml air. The FID signal was evaluated based on a two-point calibration graph. The detection limit of alcohols and ketones was also studied by a GC–MS analytical system.

### 3. Results and discussion

When deionized water was fed in at a flow-rate of 500 µl/min and air of 50–100% relative humidity

(RH) was used, there was no wetting problem of the denuder tube observed over a 1-month measuring period. Relative humidity of air had no influence on the reliability of collection efficiency of alcohols and ketones.

It is easily calculated from the known vapour pressure of water that if the sampled air is completely dry and the exit air is completely humid, up to 9.6, 18.3 and 33.6 µl/min of water can evaporate per 1 l/min sampled air at 10, 20 and 30°C and 101.325 kPa. The maximum loss of water (40.1 µl/min) has been calculated at a temperature of 30°C and a flow-rate of dry air of 1217 ml/min. During field sampling with 1 l/min air sample flow, we can arbitrarily assume an evaporation loss of 50% of these maximum values, which should lead to an influence of amount of aspirate liquid concentrate in intervals of 495.2–483.2 µl/min. An error in variable evaporation losses could be at most to below 2% error in the total flow-rate of absorption liquid and hence the computed gas-phase analyte concentrations.

In the case that the “active” wall(s) of the denuder is a perfect sink for the analyte, the collection

efficiency ( $\epsilon$ ) of the analyte in cylindrical WEDD can be described, under a constant temperature, pressure and steady-state air laminar flow-rate conditions, by a multi-exponential equation [3–5,16,17]. At constant length of denuder tube the flow-rate of air streaming through the denuder is the only factor controlling behaviour of analyte molecules within WEDD [3–5,16,17]. When we compare the theoretical collection efficiencies (Fig. 2a,b) calculated for the first member of the Gormley–Kennedy equation [16] of the investigated oxo compounds employing the Fuller, Schettler, and Giddings method (see Ref. [18]) for diffusion coefficient calculation, with the experimental values of collection efficiencies of alcohols and ketones at a range of air flow-rates of 416–1217 ml/min and at a temperature of 20°C (Fig. 3a,b), it is evident that experimental data are mostly far from the theoretical values. The collection ef-

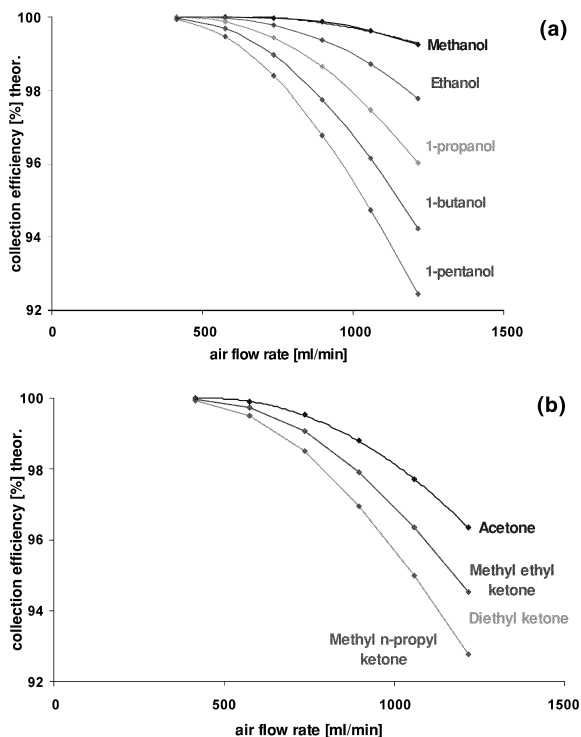


Fig. 2. (a) The theoretical collection efficiency of the alcohols in a cylindrical wet effluent diffusion denuder, at a temperature of 20°C. (b) The theoretical collection efficiency of the ketones in a cylindrical wet effluent diffusion denuder, at a temperature of 20°C.

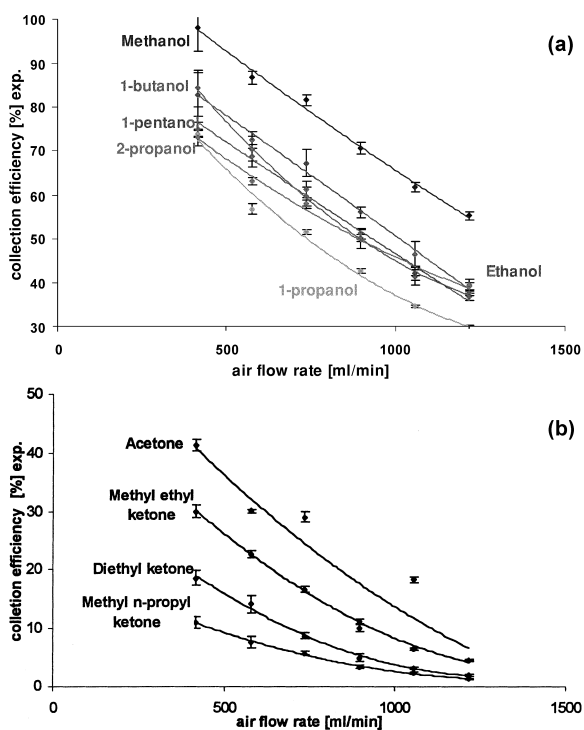


Fig. 3. (a) Experimental dependencies of the collection efficiency of the alcohols in a wet effluent diffusion denuder on flow-rate, at a temperature of 20°C. (b) Experimental dependencies of the collection efficiency of the ketones in a wet effluent diffusion denuder on flow-rate, at a temperature of 20°C.

ficiencies of alcohols are as high as  $98 \pm 1.12\%$  for methanol at a flow-rate of 416 ml/min and as low as  $36.83 \pm 0.78\%$  when 1-pentanol is the analyte at an airflow-rate of 1217 ml/min. At a temperature of 20°C, the highest collection efficiency of ketones has been measured for acetone ( $31.40 \pm 1.01\%$ ) and a flow-rate of 416 ml/min, while the lowest collection efficiency was displayed by methyl *n*-propyl ketone ( $1.32 \pm 0.07\%$ ) at a flow-rate in air 1217 ml/min. Only the behaviour of methanol more or less complies with the assumption of the expected values of the Gormley–Kennedy equation. The collection efficiency of remaining alcohols and ketones strongly depends, in contrast to highly soluble gases [19], on their Henry's constants (J. Pešková, Z. Večeřa, unpublished data).

More experimental data concerning of collection efficiency of alcohols and ketones during the mass transfer process into the cylindrical wet effluent

diffusion denuder are presented in Table 1. It is obvious that both the flow-rate of air and influence of temperature in general are the essential parameters that affect the transport of compounds from the gas phase to water within the preconcentration into WEDD. The collection efficiencies for methyl *n*-propyl ketone, dimethyl ketone, methyl ethyl ketone and 2-propanol, at a temperature of 10°C, are 25.49, 30.49, 45.30 and 81.94%, respectively. At a temperature of 30°C the collection efficiencies of those compounds drop to 3.86, 6.03, 16.89 and 64.04%. Temperature has a negligible effect on collection efficiency for some of the studied compounds

(methanol, 1-pentanol and acetone) mainly at relatively low flow-rates of air. However, it is necessary to thermostat the wet effluent diffusion denuder for field measurements.

The results indicate that water is an excellent absorption medium for preconcentration of alcohols. Water is not such a good absorption liquid in terms of the Gormley–Kennedy equation for ketones containing more than four carbons. However, the collection efficiency for methyl *n*-propyl ketone is 11.04% at a temperature of 20°C and airflow-rate of 1057 ml/min, but this value of  $\epsilon$  is still enough to enable measurement of airborne concentration of this oxo compound at the minimum detectable level (a signal-to-noise ratio of 3): 0.24  $\mu\text{g/l}$  (GC–FID). When the concentrate undergoes GC–MS analysis, the minimum detectable level can be as low as 1 ng/l.

In view of the results in Table 1, the degree of preconcentration ( $D_w = C_l/C_g$ , where  $C_l$  is the concentration of analyte leaving and  $C_g$  represents the concentration of analyte entering the WEDD) for methanol (0.5 ml/min of water, 1057 ml/min of air) is about 2100. Under the same conditions the degree of preconcentration for *n*-propyl ketone is still 233.

The reproducibility of  $\epsilon$  results was checked for GC–FID data received over a 4-day measurement period. All of the single points of the relationships (Fig. 3a,b and the data in Table 1) present a mean value of at least 20 measurements.

#### 4. Conclusion

Water was proved to be an absorption medium for the preconcentration of alcohols and ketones and has been found to be a good absorption medium for the preconcentration of alcohols from air in a cylindrical wet effluent diffusion denuder. In terms of the Gormley–Kennedy equation the absorption of ketones indicates that there was no perfect sorption. The experimental data fitted with great precision, and preconcentration in the wet effluent diffusion denuder followed by GC–FID and/or GC–MS analysis can be successfully used for the on-line determination of alcohols and/or ketones in air at concentration levels of hundreds of ng and/or a few ng per litre of sampled air, respectively, but the WEDD is necessary to thermostat.

Table 1

Collection efficiencies of alcohols and ketones in the cylindrical wet effluent diffusion denuder at three temperatures and three flow-rates of air

Compounds	Temp. (°C)	Collection efficiency (%)		
		Flow rate (ml/min)		
		416	1057	1217
Methanol	10	91.03	69.31	63.92
	20	98.03	61.74	55.18
	30	94.31	55.54	51.01
Ethanol	10	84.66	53.51	48.02
	20	82.90	46.35	39.02
	30	72.59	36.82	30.80
1-Propanol	10	78.77	42.97	37.07
	20	73.91	34.64	29.63
	30	61.02	26.94	22.69
2-Propanol	10	81.94	46.84	42.74
	20	72.97	42.21	39.39
	30	64.06	32.89	30.73
1-Butanol	10	84.25	59.26	48.66
	20	76.28	41.21	37.61
	30	68.52	30.77	26.95
1-Pentanol	10	77.91	50.82	42.30
	20	75.05	42.19	36.83
	30	74.27	29.61	24.13
Acetone	10	32.16	17.07	4.63
	20	31.40	18.26	4.58
	30	32.94	22.88	5.54
Methyl ethyl ketone	10	45.30	14.03	12.14
	20	30.00	6.4	4.53
	30	16.89	1.93	1.10
Diethyl ketone	10	30.49	11.59	9.00
	20	18.57	3.1	2.03
	30	6.03	0.69	0.38
Methyl <i>n</i> -propyl ketone	10	25.49	6.03	4.44
	20	11.04	2.33	1.32
	30	3.86	0.34	0.21

The wet effluent diffusion denuder technique and gas chromatographic analysis can be effectively used for analytical monitoring of air containing organic polar pollutants at the safety level and/or ppb (v/v) concentrations, especially in cases when there could be problems arising from the presence of aerosols (detergent industry), and where the high time-resolution of the gas concentration of alcohols and/or ketones is necessary.

### Acknowledgements

This work was supported by a grant No. 203/98/0943 from the Grant Agency of the Czech Republic.

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