Diffusion technique for the production of gas standards for atmospheric measurements

M. Gautrois*, R. Koppmann

Institut für Atmosphärische Chemie, Forschungszentrum Jülich, 52425 Jülich, Germany

Abstract

For the calibration of gas chromatographic measurements of volatile organic compounds in ambient air samples, standard gas mixtures at low concentrations are needed with high accuracy. For this purpose we developed a diffusion device combined with a dynamic dilution system. Pure liquid compounds are placed in glass vials. They diffuse through a capillary on top of each vial into a diffusion chamber flushed with synthetic air. In an additional dynamic dilution step the final concentration is adjusted with a flow of purified synthetic air to typical mixing ratios between several ppt (v/v) and ppb (v/v). The diffusion rates are determined from the mass loss of the vials. Extensive tests over 21 months showed that the diffusion rates varied little with time, between 1.4% and 3.1%, depending on the compound. The system proved to be suitable for compounds with a wide range of boiling points, from 305 K (1,1-dichlorethene) to 418 K (1,2-dimethylbenzene). The diffusion device was applied to a gas chromatographic system with a flame ionization detector and an electron-capture detector. The linearity of the diffusion device was checked with different standard mixtures with mixing ratios ranging from 0.32 ppt (v/v) (tribromomethane) to 1353 ppt (v/v) (*n*-pentane). The regression analysis of peak area versus concentration showed excellent agreement among the standards for each compound with correlation coefficients (r^2) between 0.9826 and 0.9998. The temporal stability of the diffusion device was determined from more than 270 measurements of one standard mixture. The reproducibility of the peak areas ranged between 2.2% and 12.7% depending on the compound. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds are important trace gases which influence atmospheric chemistry in many ways. The distribution of these compounds in the atmosphere – in urban areas as well as in remote regions – is very complex and their concentrations vary from a few ppt to several ppb. The most widely used technique for the measurement of volatile organic compounds (VOCs) in the atmosphere is gas chromatography combined with different detectors. The output signal of a detector is a function of either concentration or mass of an analyte. For quantitative analyses this relation has to be determined by calibration with a standard of known composition. Therefore, reproducible and accurate gaseous standard mixtures of typical ambient mixing ratios are required.

*Corresponding author.

Gaseous standard mixtures can be prepared by either static or dynamic methods. A typical static method is the microgravimetrical preparation of primary standards with concentrations between several 100 ppb (v/v) (ppbv) and some 10 ppm (v/v) (ppmv) in gas cylinders [1–5]. These primary standard mixtures have to be diluted in several steps to lower mixing ratios which often is a source of errors. Further, polar or reactive compounds, such as oxygenated and unsaturated are not stable in gas cylinders due to adsorption or chemical decomposition at the walls.

Dynamic methods for the preparation of gaseous standards make use of permeation and diffusion. Several designs of permeation tubes have been described in the literature [6–10]. Permeation tubes consist of inert polymer, e.g. fluorinated ethylene–propylene copolymer (FEP) or polytetrafluoroethylene (PTFE). These inert polymers are also suitable for reactive compounds. The permeation rates are determined by the diameters and wall thicknesses of the polymers.

Diffusion devices make use of vials containing the liquid or solid compound and a capillary on the top as diffusion path. This system has the advantage that the diffusion rate can be varied over a wide range by the dimension of diffusion capillary. The possibility to prepare hydrocarbon gas mixtures at low concentrations with a diffusion system has been suggested in the past [11–15]. An overview of the different methods is given by Namiesnik [16]. Staudt et al. described a dynamic system for producing gas mixtures with six monoterpenes with boiling points of about 433 K at lower ppb level [17].

In this paper we describe the preparation of gaseous standards at parts per trillion (pptv) level with a wide range of liquid compounds based on a diffusion device. The temporal stability of the gravimetrically determined diffusion rates of 18 compounds with boiling points ranging from 305 K (1,1-dichloroethene) to 418 K (1,2-dimethylbenzene) was investigated. The diffusion coefficients calculated from the mass loss were compared with literature values. Finally, the temporal stability of the diffusion device was examined by the gas chromatographic system which is used for the measurements of ambient air samples.
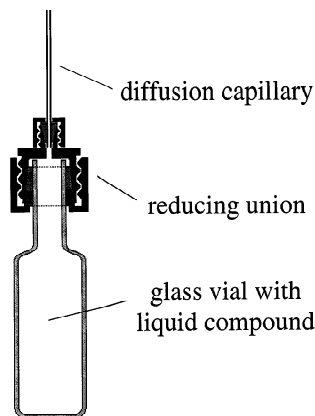

Fig. 1. Drawing of the diffusion vial.

2. Experimental

2.1. Diffusion vial

Fig. 1 shows the design of the diffusion vials ($V=4$ ml) used in this study. A stainless steel capillary is connected to the glass vial using a Swagelok reducing union ($\frac{1}{4}$ in. to $\frac{1}{16}$ in.; 1 in.$=2.54$ cm). At the glass side Vespel/Graphite ferrule is used and at the capillary side a stainless steel ferrule. The stainless steel capillaries have an internal diameter of 1 mm and lengths between 10–100 mm depending on the diffusion coefficient and vapor pressure of the compound. Initially, the glass vials are filled with 3 ml of the liquid compounds.

2.2. Diffusion chamber

The diffusion chamber is a double walled glass chamber, which is installed in an insulated transport box. The temperature in the diffusion chamber is kept constant at 298 K by flushing water between the inner and outer glass walls. The water temperature is controlled by an external thermostat (Julabo, F25-MP). Up to twenty diffusion vials can be placed into the diffusion chamber.

2.3. Preparation of gaseous standard mixtures

Fig. 2 shows a schematic drawing of the complete diffusion system for the preparation of gaseous standard mixtures. Pressurized air is passing a
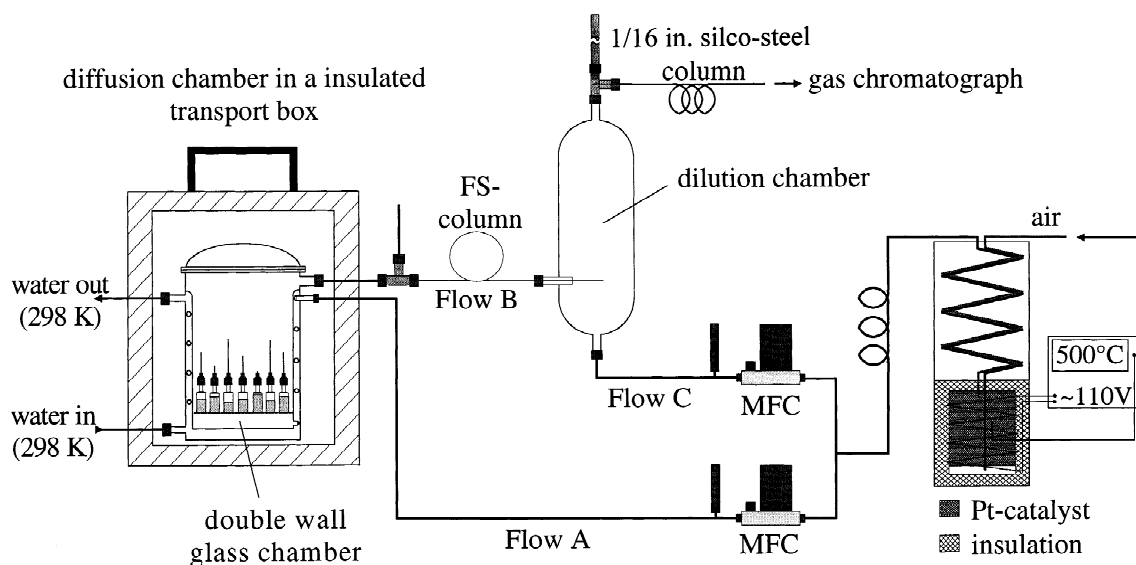
Fig. 2. Schematic drawing of the diffusion system. MFC = Mass-flow controller.

platinum catalyst at a temperature of 773 K to remove hydrocarbons and halocarbons. The air is cooled down to ambient temperature by a heat exchanger. The air flow is split into two separate flows (A and C in Fig. 2). In both lines the flow is adjusted by mass-flow controllers (Brooks, TR5850, 0–10 ml min^{-1} air and Brooks, TR5850, 0–50 ml min^{-1} air).

After passing the glass coil surrounding the diffusion chamber air flow A is flushed through the diffusion chamber from the bottom to the top, thereby passing the vials. This flow was always kept constant at 6.7 l min^{-1} to guarantee a constant pressure in the diffusion chamber and thus constant diffusion rates. The pressure in the chamber is adjusted to 160 hPa above ambient pressure by a gas split at the outlet of the chamber. Thus, the absolute pressure in the chamber varies depending on the ambient pressure. Typical mixing ratios in the air leaving the diffusion chamber were in the range of 20–900 ppbv.

Part of the flow leaving the diffusion chamber is transfered into a dilution chamber via a deactivated fused-silica column as a flow restrictor. The final concentration can now be adjusted by varying the dimension of the transfer column and/or the flow

through the diffusion chamber. In this experiment flow (B) was varied by using deactivated fused-silica columns of different internal diameters (0.10 to 0.32 mm) and lengths (0.5 to 2.5 m). Depending on the dimension of the columns the flow-rates ranged from 0.28 to 5.6 ml min^{-1}.

This small flow of air is fed into a dilution chamber with a volume of 400 ml. Inlet and outlet for the flush air (C) have different internal diameters, to avoid an increase above ambient pressure ($d_{inlet} = 3$ mm and $d_{outlet} = 7$ mm). The flow of air (C) through the dilution chamber was varied between 4 and 18 l min^{-1} leading to final concentrations in the range from sub-pptv to ppbv.

The diffusion rates (μg/min) are determined by measuring the mass loss of the compounds from the glass vials on a microbalance (Sartorius Research, type: R 160 P). The time intervals between weighings range from one day up to several months.

2.4. Chemicals

The hydrocarbons and halocarbons used for these experiments are listed in Table 1. Prior to the diffusion experiments the compounds were examined for impurities by GC–electron-capture detection

Table 1
Supplier, purity and some properties of the compounds

Compound	Supplier	Purity of the compounds (%)	Molecular mass (g mol^{-1})	Vapor pressure at 298 K in Pa [25]
Halogenated hydrocarbons				
1,1-Dichloroethene	Merck	>99	96.94	80 000
Bromoethane	Merck	>99	108.97	62 500
Dichloromethane	Sigma–Aldrich	99.9	84.93	58 200
Iodomethane	Merck	>99	141.94	53 900
Trichloromethane	Sigma–Aldrich	99.9	119.38	26 200
1,1,1-Trichloroethane	Sigma–Aldrich	>99	133.40	16 500
Tetrachloromethane	Merck	>99.8	153.82	15 200
Trichloroethene	Sigma–Aldrich	>99.5	131.39	9910
Dibromomethane	Sigma–Aldrich	>99	173.83	6120
Tetrachloroethene	Merck	>99	165.83	2420
1,2-Dibromoethane	Merck	>99	187.86	1550
Tribromomethane	Sigma–Aldrich	>99	252.73	726
Hydrocarbons				
n-Pentane	Merck	>99.5	72.15	68 300
n-Hexane	Merck	>97	86.18	20 200
Benzene	Merck	>99	78.11	12 700
n-Heptane	Merck	>99.5	100.20	6090
Toluene	Merck	>99.8	92.14	3790
1,2-Dimethylbenzene	Merck	>99.8	106.17	880

(ECD)/flame ionization detection (FID) by placing the compounds into the diffusion chamber and analyzing them individually.

2.5. Gas chromatography

The gaseous standard mixtures were analyzed with a gas chromatograph equipped with FID and ECD systems in series, which is used for measurements of ambient air samples. One thousand and forty two milliliters of the standard mixtures were cryogenically preconcentrated at 77 K on a silco-steel column packed with porous glass beads (15 cm×2 mm I.D.). Subsequently, the sample was thermally desorbed at 393 K and injected into a chromatographic column (GSC GasPro, 60 m×0.32 mm I.D.). The initial temperature was held at 2°C for 6 min and then programmed to 230°C at 5°C min^{-1}. The carrier gas (He) flow-rate was 4 ml min^{-1}. Purified nitrogen was used as make-up gas with a flow-rate of 20 ml min^{-1} for both detectors. Further details of the system are described by Ramacher et al. [18].

3. Results

3.1. Calculation of diffusion rates

The diffusion of the compounds from the glass vial into the chamber is controlled by concentration gradient over the capillary. Assuming that the gas phase in the vial is saturated and that the concentration of the vapor in the diluent gas is approximately zero, the diffusion rate is given by [12,13]

$$r = \frac{DMAP}{LRT} \cdot \ln \frac{P}{P - P_L} \tag{1}$$

where r=diffusion rate (g s^{-1}); D=diffusion coefficient at pressure p (cm^2 s^{-1}); M=molecular mass (g mol^{-1}); A=cross-sectional area of capillary (cm^2); P=total pressure (Pa); L=length of capillary (cm); R=gas constant (cm^3 Pa/mol K); T=absolute temperature (K); P_L=saturated vapor pressure of liquid (Pa).

The diffusion coefficient is pressure dependent and usually tabulated for 298 K and 101 325 Pa. The

pressure dependence of the diffusion coefficient is given by [12,13]

$$D = D_0 \cdot \left(\frac{P_0}{P} \right) \qquad (2)$$

where D_0 = diffusion coefficient at standard pressure P_0 (101 325 Pa); D = diffusion coefficient at pressure P.

Combination of Eqs. (1) and (2) yields:

$$r = \frac{D_0 P_0 M A}{LRT} \cdot \ln \frac{P}{P - P_L} \qquad (3)$$

The variation of the ambient pressure leads to a variations of the diffusion rates. To estimate the relative change of the diffusion rates we calculated these values for typical pressure extremes of 980 hPa and 1020 hPa. The pressure in the diffusion chamber is adjusted to 160 hPa above ambient pressure. Thus, the total pressure in the chamber ranged between 1140 hPa and 1180 hPa. The data compiled in Table 2 show the dependence of the diffusion rates on the total pressure. An increase of the total pressure at 40

hPa leads to decrease of 3.4–6.3% of the diffusion rates depending on the vapor pressure of the substance.

3.2. Temporal stability of diffusion rates

The temporal stability of the diffusion rates was monitored by weighing the diffusion vials in regular time intervals over a period of 21 months. For weighing intervals of less than a week we observed enhanced diffusion rates. This effect correlated with the vapor pressure of the compound. The expected mass loss for short weighing intervals can be calculated from the mean diffusion rates. The difference between determined and calculated mass losses for weighing intervals of about one day ranges from 6.5 ± 2 mg (1,1-dichloroethene) to 5 ± 35 µg (tribromomethane) depending on the vapor pressure. A possible reason for this observation is that compared to the diffusion chamber the vials are no longer at constant temperature and at lower pressure during the weighing step. This affects the diffusion rates. In the case of 1,1-dichloroethene the diffusion rates will

Table 2
Effect of total pressure on diffusion rate. The diffusion rates are given in µg min^{-1} at 298 K

Compound	114 000 Pa	118 000 Pa	Relative decrease of the diffusion rates (%)
Halogenated hydrocarbons			
1,1-Dichloroethene	28.73	26.91	6.3
Bromoethane	25.39	24.10	5.1
Dichloromethane	24.37	23.18	4.9
Iodomethane	19.26	18.36	4.7
Trichloromethane	8.89	8.55	3.9
1,1,1-Trichloroethane	9.12	8.78	3.7
Tetrachloromethane	10.04	9.67	3.6
Trichloroethene	10.07	9.72	3.5
Dibromomethane	11.52	11.12	3.5
Tetrachloroethene	5.47	5.28	3.4
1,2-Dibromoethane	4.02	3.88	3.4
Tribromomethane	2.39	2.31	3.4
Hydrocarbons			
n-Pentane	17.84	16.87	5.4
n-Hexane	9.48	9.13	3.7
Benzene	8.29	7.99	3.6
n-Heptane	7.85	7.57	3.5
Toluene	5.10	4.92	3.4
1,2-Dimethylbenzene	1.15	1.11	3.4

decrease by about 25% for a ambient temperature of 293 K and increase by about 35% for atmospheric pressure of 1013 hPa. Since the duration of the weighing procedure is in the order of 30 min, this will have only a minor influence. On the other hand, the gas phase in the diffusion vial expands by 16% when opening the diffusion chamber. This expansion leads to a mass loss of about 1 mg 1,1-dichloroethene. However, Fig. 3 shows that both effects become negligible for weighing intervals of more than a week.

Table 3 lists the two groups of compounds in the order of boiling points and gives the mean diffusion rates with their variability for weighing intervals of more than one week. The variability of the diffusion rates was less than 3.1% for all compounds. Generally, the reproducibility was better for compounds with higher diffusion rates. The observed stability of the diffusion rates is always better than the calculated variability depending on the total pressure in the chamber (Table 2). Thus, the variation of the ambient pressure has no noticeable effects on the stability of the diffusion rates.

Table 3
Mean and standard deviation of diffusion rates based on 30 weighings over a period of 21 months

Compound	Capillary length (mm)[a]	Mass loss ($\mu g\ min^{-1}$)
Halogenated hydrocarbons		
1,1-Dichloroethene	90	24.39±1.4%
Bromoethane	65	25.28±1.6%
Dichloromethane	50	23.49±1.7%
Iodomethane	100	18.98±1.7%
Trichloromethane	60	8.75±1.6%
1,1,1-Trichloroethane	35	8.10±1.5%
Tetrachloromethane	35	8.60±1.5%
Trichloroethene	20	7.59±2.2%
Dibromomethane	15	8.02±2.1%
Tetrachloroethene	10	3.05±2.0%
1,2-Dibromoethane	10	2.27±2.0%
Tribromomethane	10	1.48±2.0%
Hydrocarbons		
n-Pentane	60	18.56±1.8%
n-Hexane	25	8.54±1.5%
Benzene	20	6.36±2.0%
n-Heptane	10	4.64±2.0%
Toluene	10	3.04±2.0%
1,2-Dimethylbenzene	10	0.73±3.1%

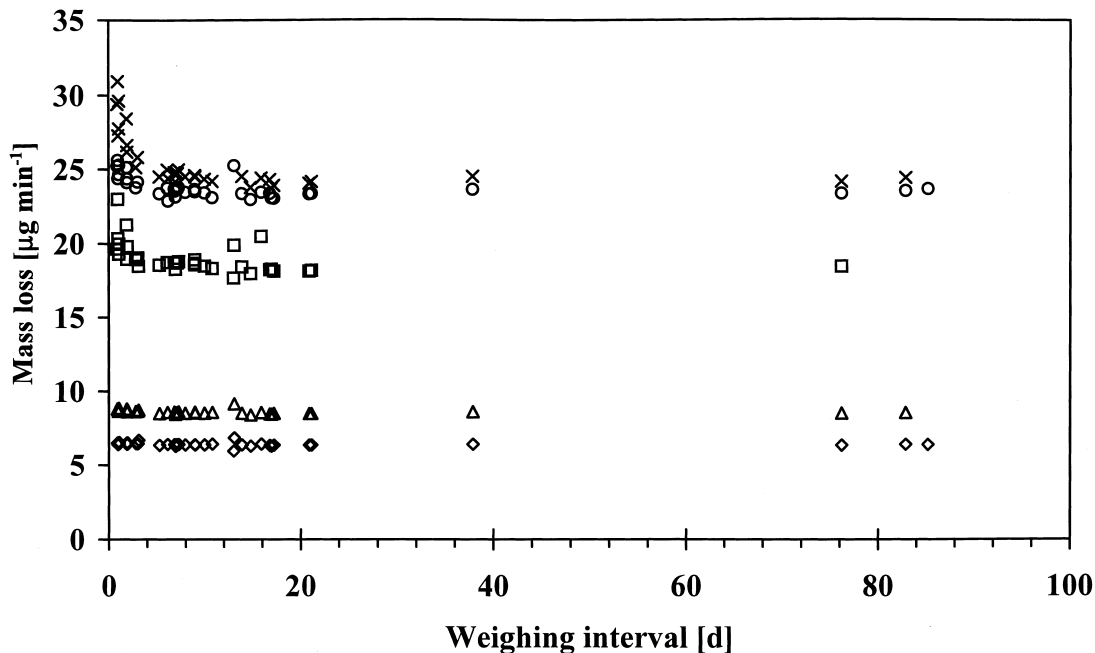[a] All capillaries have an inner diameter of 1 mm.

Fig. 3. Relationship between the mass loss and the weighing interval (×, 1,1-dichloroethene; □, *n*-pentane; ○, dichloromethane; △, *n*-hexane; ◇, benzene).

During the experiment the diffusion vials had to be refilled several times. Our results show that the diffusion rates were not significantly influenced by this manipulation.

In principle, our experiment allows the calculation of diffusion coefficients. For compounds with low boiling points we assume that the specific compound in the gas space of the vial is at saturated vapor pressure. Thus, the diffusion rate is only determined by the diffusion through the capillary. For compounds with higher boiling points we expect lower diffusion rates due to the design of diffusion vials. In this case the diffusion through the capillary is faster than the evaporation. This leads to a concentration gradient in the gas space and the partial pressure at the capillary is lower than the saturated vapor pressure. The calculated diffusion coefficients are summarized in Table 4 and compared with values are given in the literature [16–20] at standard conditions of 298 K and 101 325 Pa. The diffusion coefficients for the light volatile compounds up to 1,1,1-trichloroethane agree better than 10% with the litera-

ture data. As discussed above, for the higher boiling compounds the deviations increase.

3.3. Gaschromatographic test of the system

The gaseous standard mixtures were tested for reproducibility and stability with the GC–ECD/FID system, which is used for the measurements of ambient air samples. The linearity of the system was checked by injecting six different standard mixtures with concentrations ranging over two orders of magnitude. The different concentrations were adjusted by varying of the split ratios and the air flow through the dilution chamber. Table 5 gives the mean and standard deviation (1σ) of the adjusted air flows through the diffusion chamber, fused-silica column and dilution chamber. The split ratio describes the ratio from the flow (B) through the column to the flow (A) through the diffusion chamber. This parameter was varied between $4.04 \cdot 10^{-5}$ and $8.03 \cdot 10^{-4}$ by using different fused-silica column. The concentrations of the gaseous mixture

Table 4
Comparison of experimentally determined diffusion coefficients with literature data. All values are given in $cm^2 \ s^{-1}$ normalized to 298 K and 101 300 Pa

Compound	This work[a]	Lugg [19]	Cowie [21]	Watts [20,22]	Barr [23]
Halogenated hydrocarbons					
1,1-Dichloroethene	0.1026±0.0014	–	–	–	0.1144
Bromoethane	0.1029±0.0017	0.0989	–	–	–
Dichloromethane	0.1047±0.0018	0.1037	0.1042	0.1016	–
Iodomethane	0.1129±0.0026	–	–	–	–
Trichloromethane	0.0903±0.0014	0.0888	0.0862	0.0888	
1,1,1-Trichloroethane	0.0728±0.0011	0.0794	–	0.0793	–
Tetrachloromethane	0.0732±0.0011	0.0828	0.0759	0.0759	–
Trichloroethene	0.0680±0.0015	0.0875	–	0.0800	–
Dibromomethane	0.0671±0.0014	–	–	–	–
Tetrachloroethene	0.0458±0.0009	0.0797	–	0.0711	–
1,2-Dibromoethane	0.0472±0.0009	–	–	–	–
Tribromomethane	0.0490±0.0010	0.0767	–	–	–
Hydrocarbons					
n-Pentane	0.0918±0.0029	0.0842	–	–	0.0856
n-Hexane	0.0680±0.0011	0.0732	–	–	–
Benzene	0.0738±0.0015	0.0932	–	–	–
n-Heptane	0.0451±0.0009	–	–	–	–
Toluene	0.0521±0.0010	0.0849	–	–	–
1,2-Dimethylbenzene	0.0476±0.0015	0.0727	–	–	–

[a] The errors are calculated based on the standard deviations of the diffusion rates.

Table 5
Mean and standard deviation of air flows through the diffusion chamber, fused-silica column and dilution chamber

Compound	Flow through the diffusion chamber (ml min^{-1})[a]	Flow through the fused-silica column (ml min^{-1})[a]	Split ratios	Flow through the dilution chamber (ml min^{-1})[a]	Total dilution factor (min ml^{-1})
Dilution 1	6894±42	2.82±0.045	4.09·10^{-4}	10 503±71	3.89·10^{-8}
Dilution 2	6823±51	2.75±0.047	4.04·10^{-4}	17 564±71	2.30·10^{-8}
Dilution 3[b]	6913	0.28	4.04·10^{-5}	17 800	2.27·10^{-9}
Dilution 4	6932±32	2.83±0.032	4.08·10^{-4}	4115±20	9.92·10^{-8}
Dilution 5	6903±50	5.55±0.072	8.03·10^{-4}	4123±6	1.95·10^{-7}
Dilution 6	6883±24	5.51±0.026	8.00·10^{-4}	14 923±15	5.36·10^{-8}

[a] All values are given for 298 K and 101 300 Pa.
[b] One measurement only.

were adjusted by the flow (C) through the dilution chamber. The total dilution factor given by Eq. (4) ranged between $2.27·10^{-9}$ and $1.95·10^{-7}$.

$$\lambda = \frac{j_B}{j_A j_C} \qquad (4)$$

where λ = total dilution factor (min ml^{-1}); j_A = flow through the diffusion chamber (ml min^{-1}); j_B = flow through the fused-silica column (ml min^{-1}); j_C = flow through the dilution chamber (ml min^{-1}).

The concentrations of the gaseous mixture can be calculated with the equation

Table 6
Concentrations of the tested gaseous standard mixtures pmol mol^{-1} (ppt) and the detection response and detection limit (3σ) of FID calculated by linear regression

Compound	Dilution 1	Dilution 2	Dilution 3	Dilution 4	Dilution 5	Dilution 6	Detector response[c] (μV s pg^{-1})	Coefficient of correlation (r^2)	Detection limit (ppt)
Electron-capture detection									
1,1-Dichloroethene[a]	235	141	14	611	1200	330	83.3±2.8%	0.9923	2.3
Iodomethane[b]	127	76	7.5	328	644	177	–	–	–
Dichloromethane[b]	259	155	15.3	670	1316	362			
Trichloromethane[a]	69	41	4.1	178	349	96	891±1.5%	0.9978	1.5
Tetrachloromethane[b]	53	31	3.1	136	266	73	–	–	–
Trichloroethene[a]	56	33	3.3	143	281	77	1232±1.0%	0.9990	2.3
Dibromomethane[b]	43	27	2.6	115	225	62	–	–	–
1,1,1-Trichloroethane[b]	57	34	3.4	147	289	80	–	–	–
Tetrachloroethene[a]	17	10	1.0	44	87	24	5566±1.7%	0.9970	0.5
Tribromomethane[b]	5.5	3.3	0.32	14	28	7.6	–	–	–
1,2-Dibromoethane[b]	11	6.8	0.67	29	57	16	–	–	–
Flame ionisation detection									
1,1-Dichloroethene[a]	235	141	14	611	1200	330	83.6±1.4%	0.9981	11
n-Pentane[a]	243	160	16	689	1353	372	297±1.2%	0.9985	6.7
Iodomethane[a]	127	76	7.5	328	644	177	22.0±4.3%	0.9826	45
Dichloromethane[a]	259	155	15	670	1316	362	40.0±1.6%	0.9975	41
n-Hexane[a]	93	56	5.5	241	472	130	248±0.6%	0.9996	13
n-Heptane[a]	43	26	2.6	113	222	61	229±1.8%	0.9967	5.3
Benzene[a]	77	46	4.6	199	391	108	295±1.0%	0.9989	9.4
Toluene[a]	31	19	1.8	81	158	44	287±0.4%	0.9998	7.4

average error of the detector response = 1.6%

[a] The detector response is linear over the entire range of concentrations injected.
[b] The detector response is non linear over the range of concentrations injected.
[c] Slope of the linear regression with relative error of the slope.

$$c = \frac{r' \lambda N_A}{MN} \cdot 10^6 \qquad (5)$$

where c = concentrations of the gaseous mixture (ppt); r' = gravimetrically determined diffusion rate of the compound (μg min^{-1}); λ = total dilution factor (min ml^{-1}); N_A = Avogadro constant ($6.02205 \cdot 10^{23}$ mol^{-1}); M = molecular weight (g mol^{-1}); N = number density ($2.46147 \cdot 10^{19}$ ml^{-1}).

The analysis time on the GSC GasPro capillary column was 56 min. The quantification of bromoethane is difficult because it elutes with the water peak. For 1,2-dimethylbenzene, only the highest concentrated standard mixture was above the detection limit. Thus, both compounds were excluded in the following discussion. For other compounds, the concentrations of the six gaseous standard mixtures and the results of the linear regression analyzes are shown in Table 6. The mixing ratios ranged from 0.32 ppt (tribromomethane) to 1353 ppt (*n*-pentane). The FID response for each compound and the ECD response for four compounds were calculated from the slope of linear regressions of the gravimetrically determined concentration versus peak area. For the other compounds the ECD detector response is non linear in the tested range of mixing ratios. As an example the ECD and FID responses of dichloromethane and iodomethane are shown in Fig. 4. Similar results were obtained for the other halocarbons. This behavior was also reported by Rudolph et al. [24]. Thus, ECD is not suitable to test the linearity of the diffusion system, except for 1,1-dichlorethane, trichloromethane, trichloroethene and tetrachloroethene. Therefore, we use the FID response which has a significantly wider range of linearity. The agreement between the different standard mixtures is good with a correlation coefficient (r^2) between 0.9826 and 0.9998, and the average error of the detector response for all compounds is 1.6%.

The stability of the diffusion device was monitored by continuous measurements over a period of 28 days. The results of more than 270 measurements with constant mixing ratios of the standard mixture are listed in Table 7. The reproducibility of the peak areas are better than 10% for all ECD measurements. For FID measurements, the reproducibility ranged
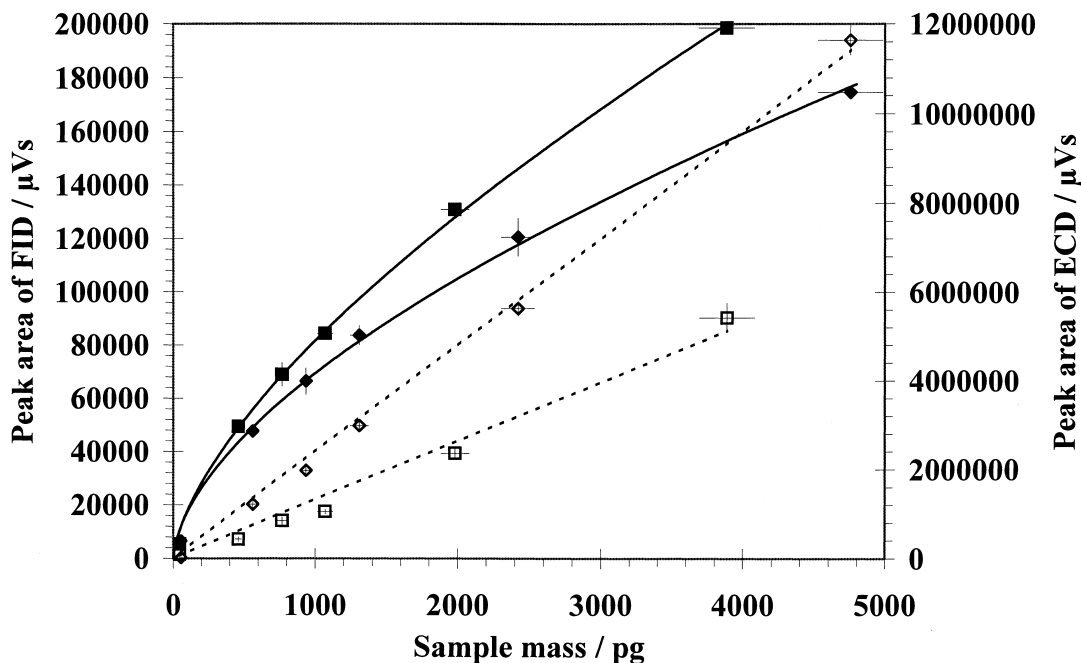

Fig. 4. Plot of sample mass versus the peak area at FID and ECD for two compounds including linear correlations as dashed line (mean value±standard deviation). The filled symbols give peak areas at ECD and open symbols give peak areas at FID: □ and ■, iodomethane; ◇ and ♦, dichloromethane. The ECD signals of dichloromethane were multiplied by a factor of 30.

Table 7
Stability of the diffusion device with constant mixing ratios

Compound	Mixing ratio (ppt)	Mean peak area (μV s)	SD
Electron capture detection			
1,1-Dichloroethene	235	68 366	3.7%
Iodomethane	127	4 149 094	2.4%
Dichloromethane	259	132 337	6.6%
Trichloromethane	69	285 948	7.6%
Tetrachloromethane	53	2 769 406	3.5%
Trichloroethene	56	356 895	2.2%
Dibromomethane	43	1 463 159	3.8%
1,1,1-Trichloroethane	57	954 124	9.8%
Tetrachloroethene	17	628 671	4.4%
Tribromomethane	5.5	85 310	5.3%
1,2-Dibromoethane	11	126 572	6.3%
average standard deviation=5.1%			
Flame ionisation detection			
1,1-Dichloroethene	235	74 298	4.5%
n-Pentane	243	198 866	5.7%
Iodomethane	127	11 699	12.7%
Dichloromethane	259	33 152	6.7%
n-Hexane	93	78 059	4.5%
n-Heptane	43	37 216	5.1%
Benzene	77	62 393	6.5%
Toluene	31	32 042	7.7%
average standard deviation=6.7%			

between 4.5% and 12.7%. The average standard deviations of both detectors with 5.1% and 6.7% are predominantly determined by the variability of the GC system.

4. Conclusion

The results of this study show that a diffusion device as described here is a efficient method for the production of gaseous standards for the calibration of GC measurements of ambient air samples. The diffusion rates are stable over a period of 21 months for a variety of liquid compounds with a wide range of boiling points. The standard deviation of the diffusion rates ranged between 1.4% and 3.1% over the whole time period. The diffusion rates were not affected by manipulations such as refilling of the diffusion vials or weighing at intervals of more than one week. Standard mixtures with mixing ratios from less than 1 ppt to several ppb can be produced with high accuracy. The diffusion device was tested with

a GC–ECD/FID system. The reproducibility of the peak areas for both detectors ranged between 2.2% and 12.7% depending on the compound.

A slightly modified diffusion system was also successfully tested with reactive compounds such as monoterpenes and sesquiterpenes. For these compounds diffusion vials with glass capillaries are used.

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