



## Diffusion technique for the generation of gaseous halogen standards

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### ABSTRACT

Halogens are known to play an important role in the tropospheric ozone-depletion chemistry and are of special interest because of their influence on the atmospheric oxidation capacity. In this paper, we investigate the application of a capillary diffusion technique for the generation of gaseous halogen standards like Br<sub>2</sub>, IBr, ICl and I<sub>2</sub>. The influence of capillary dimension (i.e. length and inner diameter), ambient pressure and headspace volume of the diffusion vessel on the test gas output has been evaluated. The experimental output rates are determined from the mass loss of the analyte vessel on a regular schedule and compared with their respective theoretical predictions. We also demonstrate that a 1,3,5-trimethoxybenzene-coated diffusion denuder is capable of collecting gaseous ICl quantitatively, which provides an attractive alternative for the rapid determination of the output of test gas devices. The output rates of ICl measured by the denuder method are in close agreements with the data obtained by the gravimetric method.

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### 1. Introduction

Halogens are very reactive chemical compounds that are known to play an important role in a wide variety of atmospheric processes such as ozone depletion in the polar boundary layer and new particle formation in the coastal boundary layer ([1–4] and references therein). Of special interest in this field is the photolysis of halogen atom precursors (e.g. dihalogens X<sub>2</sub> or XY, where X, Y denotes different halogen atoms), which leads to rapid production of halogen atoms whose main fate is to react with ozone, forming XO radicals and consequently influencing the atmospheric photooxidant budget as well as the formation of cloud condensation nuclei by chain reactions involving halogen atoms [1]. The atmospheric mixing ratios of most of these dihalogens vary widely throughout coastal areas and polar regions and the typical values are supposed to be at the level of parts-per-trillion (ppt) or subppt ([1] and references therein). However, still concentration data on the dihalogens are rare (even unavailable for ICl and IBr so far), which leaves many key processes related to atmospheric halogen chemistry open [1–3].

One of the critical steps associated with the development of analytical procedures to measure gaseous compounds in air is the generation of known and reproducible gaseous standards at typical ambient mixing ratios. Gaseous standards are essential for the verification of reliability of either sampling methods, multi-step analytical procedures or online instruments. Therefore, it is

desirable to have a highly precise gas generation source to minimize potential analytical errors. Several techniques are currently available for the preparation of gaseous standards and these are generally classified as static and dynamic methods [5–11]. The former [5–7], which involves the dilution of a concentrated standard or a pure compound to a defined gas volume, has the advantage of ease of operation; however, for certain compounds it lacks reliability mainly due to the possible adsorption or reaction of constituents on the container walls, especially at low concentration levels [5]. For these compounds dynamic methods [8–11], including permeation and diffusion techniques, provide more reliable concentrations of the compounds of interest. In these techniques the test gas concentration is controlled by the constant diffusion or permeation of the compound of interest into a diluting gas flow. By selecting suitable diffusion (i.e. capillaries) or permeation barriers (i.e. membranes) a low concentration of the gaseous standard with a wide concentration range is attainable. Especially the capillary diffusion-based method has often been used for the production of gaseous standards of volatile and semi-volatile organic compounds [9–11]. An overview of the different methods is given by Namiesnik [12].

In this work, we describe for the first time the generation of inorganic gaseous standards of halogens based on a capillary diffusion device. The stability of the gas source and the effects of capillary dimensions and headspace volume of the diffusion vessel on the output rates of different halogens are evaluated. Besides gravimetric determination of the test gas output from the capillary device, a diffusion denuder sampling system combined with gas chromatography–mass spectrometry (GC–MS) [13], which is capable of measuring gaseous dihalogen species, is used for the rapid determination of the output rate of ICl.

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## 2. Experimental

### 2.1. Reagents and materials

ICl, IBr, I<sub>2</sub>, Br<sub>2</sub>, 1,3,5-trimethoxybenzene (1,3,5-TMB), and 2,4,6-tribromoanisole were obtained from Aldrich (Steinheim, Germany). Ethyl acetate was obtained from Fluka (Steinheim, Germany). All other chemicals were of analytical reagent grade. 1-Iodo-2,4,6-trimethoxybenzene (1-iodo-2,4,6-TMB) was not commercially available and has been synthesized for the purpose of quantification [14]. The synthetic procedure was as follows: to 15 mL of 0.2 mol L<sup>-1</sup> 1,3,5-TMB aqueous solution, 381 mg of finely powdered I<sub>2</sub> was added. After the mixture was stirred at 50 °C for a few minutes, 30% aqueous solution of H<sub>2</sub>O<sub>2</sub> (1.8 mmol) and a drop of 40% H<sub>2</sub>SO<sub>4</sub> were introduced. The reaction mixture was stirred at 50 °C until iodine consumption. The product was extracted with 30-mL CH<sub>2</sub>Cl<sub>2</sub> and then washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5%, 40 mL), and dried over anhydrous MgSO<sub>4</sub>. Pure products were isolated by SiO<sub>2</sub> column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as mobile phase. The purity of 1-iodo-2,4,6-TMB was 99.3% detected by GC–MS.

### 2.2. Construction, operation and evaluation of the gas standard source

The design of the assembled diffusion devices ( $V = 2.24$  mL) used in this study is shown in Fig. 1A. A certain amount of halogen compounds of interest was filled into the vessel to which a deactivated fused capillary was connected. The length and inner diameter of the diffusion capillaries ranged from 1.0 to 20.0 cm and from 0.1 to 2.15 mm, respectively. The diffusion device was placed at the bottom of a double-walled glass chamber (Fig. 1B). The temperature in this diffusion chamber was kept at  $25.0 \pm 0.1$  °C using thermostated

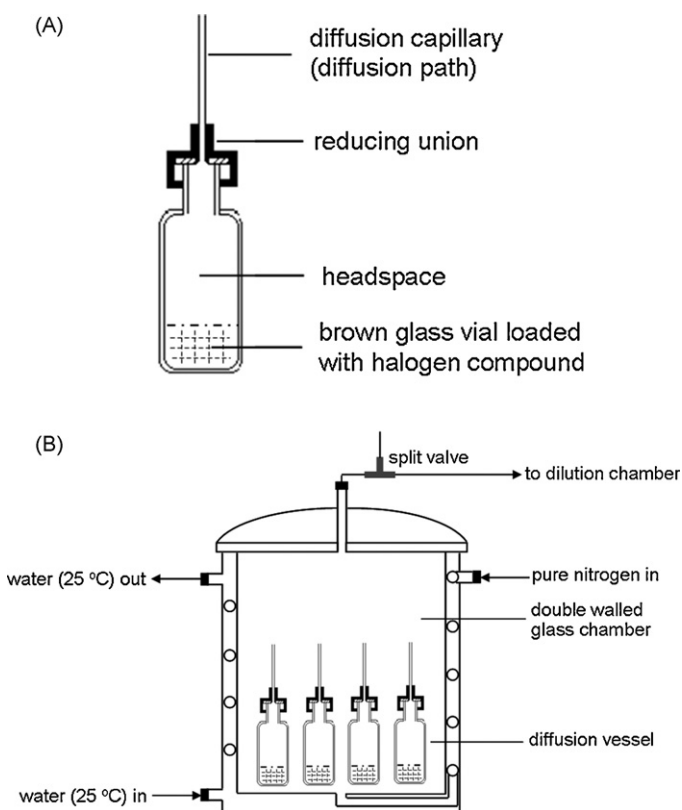


Fig. 1. Schematic diagram of the design of capillary diffusion vessel (A) (modified from [13]) and the gas standard generation system (B).

water. Nitrogen gas was flushed continuously through the diffusion chamber from the bottom to the top at a constant flow rate. The outlet of the diffusion chamber was connected to a split valve. Therefore, only part of the gaseous compound was fed into a 500-mL three-neck dilution chamber. Here, another nitrogen flow was introduced for dilution of the analyte to the concentration range needed. The whole experimental system was protected from any light by aluminium foil to avoid complications from the photodissociation of halogen compounds.

The output of the test gas (output or loss rate) was determined by periodically measuring the mass loss of the analyte vessel on a microbalance (Precisa XB120A, Switzerland). In addition to this gravimetric approach, a denuder-based method [13] was also used for the measurements of output rate of the halogen compounds.

### 2.3. Sample collection and preparation (denuder method)

Brown borosilicate glass tubes (6 mm i.d.) with a length of 50 cm were used for the preparation of denuders. 1.5 mmol L<sup>-1</sup> 1,3,5-TMB dissolved in methanol was used as coating solution. Six 500  $\mu$ L-portions of the solution were alternately pipetted into both openings of the glass tube. During the coating procedure the tubes were rotated and flushed with nitrogen for drying (flow rate 0.5 L min<sup>-1</sup>). Afterwards, the coated denuders were sealed with polypropylene (PP) end-caps and stored in the refrigerator until sampling.

The sampled gas entered the denuder through a subduction zone (uncoated glass tube, 6 mm i.d.  $\times$  length 3–18 cm depending on the gas flow) which ensured laminar flow conditions. A membrane pump was located downstream of the denuder to adjust the sampling flow rate. The sampling time was 10–20 min at a typical flow rate of 500 mL min<sup>-1</sup>. Three to five samples were taken for each measurement.

After sampling the coatings were eluted with five 2.0 mL-portions ethanol/ethyl acetate (1:1, v/v). Afterwards, 100  $\mu$ L of 2,4,6-tribromoanisole (internal standard, 6.0 mg L<sup>-1</sup> in ethyl acetate) was added into the eluate. The mixture was concentrated almost to dryness with a gentle stream of purified nitrogen (99.999%) and then redissolved in 100  $\mu$ L ethyl acetate.

### 2.4. GC–MS analysis

For the chromatographic analysis a Finnigan GC–MS (Trace GC/PolarisQ, Rodano, Italy) with a fused-silica capillary column (30 m  $\times$  0.25 mm i.d.,  $d_f$ : 0.25  $\mu$ m, Rtx<sup>®</sup>-5MS, Restek Co., Bad Homburg, Germany) was used. High-purity helium (99.999%) was used as a carrier gas at a constant flow of 1.0 mL min<sup>-1</sup>. One microliter of sample solution was introduced and the injection was done in the splitless mode (splitless time, 1.0 min) with a deactivated splitless injection glass liner that contained no glass wool. The temperature of the injector was set to 250 °C and the transfer line was set to 300 °C. The GC oven was programmed as follows: initial temperature 90 °C (hold 3 min), 30 °C min<sup>-1</sup> to 220 °C (hold 3 min). The mass spectrometer was operated in the electron impact (EI) mode (70–eV). A solvent delay of 4.5 min preceded the MS spectra acquisition and acquisition was in full scan mode at a mass range of 45–450 amu.

## 3. Results and discussion

### 3.1. Test gas output

The diffusion process in the assembled diffusion device involves the evaporation of analyte of interest from a liquid (or solid) reservoir into the headspace volume followed by the diffusion of the vapor through the capillary into the double-walled glass chamber.

**Table 1**  
Difference between calculated and measured output rate of different halogen species: dependence of capillary dimension<sup>a</sup>.

| Analyst         | Saturation vapor pressure (kPa) | Capillary length (cm) | Capillary inner diameter (mm) | Calculated output rate <sup>b</sup> (ng s <sup>-1</sup> ) | Measured output rate <sup>c</sup> (ng s <sup>-1</sup> ) | Factor (measured/calculated output) |
|-----------------|---------------------------------|-----------------------|-------------------------------|---|---|-------------------------------------|
| Br <sub>2</sub> | 28.69 <sup>d</sup>              | 2.5                   | 0.53                          | 209   | 1639 ± 116 (9)  | 7.84                                |
|                 |                                 | 2.5                   | 2.15                          | 3438  | 3571 ± 202 (6)  | 1.04                                |
| ICl             | 4.05 <sup>e</sup>               | 2.5                   | 0.10                          | 0.83 <sup>f</sup>   | 41.9 ± 2.3 (6)  | 50.5                                |
|                 |                                 | 5.0                   | 0.10                          | 0.42 <sup>f</sup>   | 25.2 ± 1.5 (9)  | 60.8                                |
|                 |                                 | 10.0                  | 0.10                          | 0.21 <sup>f</sup>   | 18.5 ± 1.6 (12)   | 89.0                                |
|                 |                                 | 20.0                  | 0.10                          | 0.10 <sup>f</sup>   | 12.4 ± 1.6 (6)  | 119                                 |
|                 |                                 | 2.5                   | 0.53                          | 23.3 <sup>f</sup>   | 109 ± 7 (12)  | 4.70                                |
|                 |                                 | 5.0                   | 0.53                          | 11.7 <sup>f</sup>   | 68.6 ± 4.9 (6)  | 5.88                                |
|                 |                                 | 10.0                  | 0.53                          | 5.83 <sup>f</sup>   | 37.7 ± 1.5 (8)  | 6.47                                |
|                 |                                 | 20.0                  | 0.53                          | 2.92 <sup>f</sup>   | 21.4 ± 1.4 (8)  | 7.32                                |
| IBr             | 1.01 <sup>e</sup>               | 2.5                   | 1.15                          | 110 <sup>f</sup>  | 117 ± 4 (6)   | 1.07                                |
|                 |                                 | 2.5                   | 0.53                          | 7.59  | 22.2 ± 1.1 (6)  | 2.92                                |
|                 |                                 | 2.5                   | 1.15                          | 35.7  | 38.2 ± 1.5 (6)  | 1.07                                |
| I <sub>2</sub>  | 0.041 <sup>g</sup>              | 4.5                   | 0.32                          | 0.0705  | 0.867 ± 0.075 (9)                                       | 12.3                                |
|                 |                                 | 2.0                   | 0.53                          | 0.435   | 0.996 ± 0.052 (21)                                      | 2.29                                |
|                 |                                 | 1.0                   | 0.53                          | 0.87  | 1.21 ± 0.05 (21)  | 1.39                                |
|                 |                                 | 2.5                   | 1.15                          | 1.64  | 1.67 ± 0.04 (6)   | 1.02                                |

<sup>a</sup> Headspace volume ~1.5 mL.<sup>b</sup> Diffusion coefficients calculated by Fuller–Schettler–Giddings method (except ICl) and saturation vapour pressure listed in the table are used for the theoretical calculation of output rate.<sup>c</sup> Mean ± SD, data in the bracket indicates the number of replicates.<sup>d</sup> Calculated by the Antoine equation using the Antoine coefficients published in [21].<sup>e</sup> Obtained from [22].<sup>f</sup> Average of calculated and measured (0.103 cm<sup>2</sup> s<sup>-1</sup>, this work) diffusion coefficient is used.<sup>g</sup> Obtained from [23].

The output rate can be controlled by the length and diameter of the capillary as well as the temperature in the capillary diffusion device and is given by [15,16].

$$r = \frac{D_0 P_0 M}{RT} \times \frac{A}{l} \times \ln \frac{P}{P-p} \quad (1)$$

where  $r$  (g s<sup>-1</sup>) is the output rate;  $D_0$  (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient at standard pressure  $P_0$  (101 kPa);  $M$  (g mol<sup>-1</sup>) is the molecular weight of vapor;  $P$  (kPa) is the total pressure in the double-walled glass chamber;  $p$  (kPa) is the partial pressure of the diffusing vapor at the absolute temperature  $T$  (K);  $R$  (cm<sup>3</sup> kPa mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant;  $A$  (cm<sup>2</sup>) and  $l$  (cm) are the cross-sectional area and length of the diffusion capillary, respectively. The diffusion coefficient of individual compounds can be either calculated by using the Fuller–Schettler–Giddings method [17–19] or experimentally determined. Also the values of the vapour pressures of the compounds of interest can be obtained by either the Antoine equation estimation [20] or by experimental measurements.

### 3.1.1. Comparison of measured and theoretical output rates

The diffusion equation (Eq. (1)) is valid only if the partial pressure of the analyte is low in the dilution gas and that the saturation partial pressure in the capillary diffusion vessel is maintained constant. In practice, the variation of the total pressure, which cannot be controlled in an open system as used here, has an additional effect on the actual test gas output and might result in differences between the theoretical predictions and practical observations. Therefore, the output rate  $r$  has to be determined by monitoring the mass loss of the analyte vessel on a regular schedule (namely, by a

gravimetric method). Table 1 lists the measured and calculated output rates of ICl, IBr, Br<sub>2</sub>, and I<sub>2</sub>. It can be seen from this table that the experimental values are in close agreements with their respective theoretical predictions with a factor of 1.02–1.07 when diffusion capillaries with large inner diameters are used (i.e. 1.15 mm i.d. for ICl, IBr, and I<sub>2</sub>, and 2.15 mm i.d. for Br<sub>2</sub>). In a previous work focussing on semi-volatile organic compounds by Possanzini et al. [10], a good agreement was also found between the calculated and tested output rates when capillaries with an inner diameter of 0.7–1.0 mm were used. However, when smaller capillaries (e.g. 0.53 mm i.d.) were applied to the halogen species investigated here, the measured test gas output was much greater than the theoretical value (see Table 1). This phenomenon can be attributed to the influence of ambient pressure variation on the test gas output. During an ambient pressure drop (e.g. by meteorological variations) the output of the test gas will not only be governed by diffusion of the test gas through the capillary, but the resulting volume variations within the diffusion device will force a certain amount of saturated vapour to leave the test gas vessel, i.e., the saturated vapor will eject through the capillary leading to enhanced output. Obviously, this effect has a larger influence on smaller test gas output; however, the inner volume of the capillary (or more precisely the ratio of the capillary volume to the headspace volume of the capillary diffusion vessel (see below)) also plays a role.

The effect of the headspace volume of the diffusion vessel on the output rate was also investigated. This set of experiments was focused on ICl and I<sub>2</sub>, representing one more volatile and one less volatile analyte. As can be seen in Table 2, the output rates of both ICl and I<sub>2</sub> are independent of the headspace volume when a 1.15 mm i.d. capillary is used. However, when a 0.53 mm i.d. capillary is used

**Table 2**  
Effect of headspace volume of the diffusion vessel on the output rate.

| Analyte        | Capillary inner diameter (mm) | Capillary length (cm) | Measured output rate (ng s <sup>-1</sup> ) |                          | Difference (%) |
|----------------|-------------------------------|-----------------------|--|--------------------------|----------------|
|                |                               |                       | Headspace volume ~1.5 mL                   | Headspace volume ~0.5 mL |                |
| ICl            | 0.53                          | 10.0                  | 37.7                                       | 22.6                     | 66.7           |
|                | 1.15                          | 2.5                   | 117  | 113                      | 3.4            |
| I <sub>2</sub> | 0.53                          | 2.0                   | 0.996                                      | 0.796                    | 25.1           |
|                | 1.15                          | 2.5                   | 1.67                                       | 1.63                     | 2.4            |

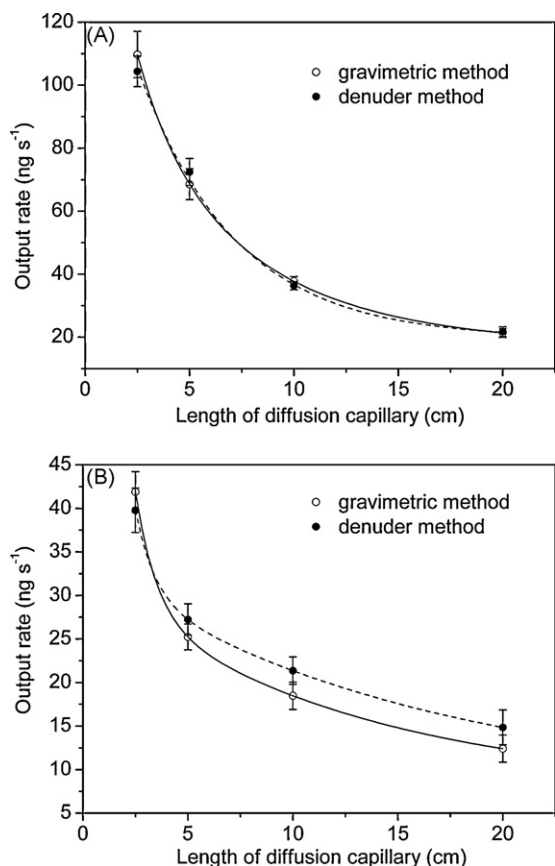


Fig. 2. The output rate of ICl as a function of length of capillary with 0.53 mm i.d. (A) and 0.10 mm i.d. (B).

the output rate obtained from 1.5-mL headspace volume is higher than the value obtained from 0.5-mL headspace volume for both ICl and I<sub>2</sub>. This observation is in agreement with the influence of ambient pressure variations on the test gas output as discussed above.

### 3.1.2. Effect of capillary length on the output rate and the stability of the gas source

Based on these results, it is obvious that a test gas output close to the theoretically calculated value can be achieved only if a diffusion capillary with relatively large dimensions is applied. In such case, however, the output of the gaseous standards of halogens is relatively high. A sequential large-volume dilution of the gaseous standards produced is therefore required to get low concentrations and to match the typical ambient mixing ratios of halogens. Therefore, despite the increasing differences between theoretical and practical output rates, diffusion capillaries with longer length and smaller diameter are still useful for the generation of standard gas mixtures. Consequently, we further tested the output rate of ICl (whose vapor pressure is in the median among the halogen compounds investigated here) using 0.53 mm i.d. and 0.10 mm i.d. capillaries with different lengths. The output rates were measured by both methods (gravimetric and denuder method). For the measurements by the denuder method, samples were collected in the regular intervals between weighings. Fig. 2A shows the output rate of ICl as a function of the length of a 0.53 mm i.d. capillary. With the increase of capillary length from 2.5 to 20 cm, the output rate decreased significantly. The measured values by the gravimetric method are very close to the values by denuder measurements with differences ranging from 1.7% to 5.5%, indicating that both gravimetric and denuder methods are effective approaches for the

determination of output rates of gaseous standard produced by the capillary diffusion technique. However, it should be noted that gravimetry is a more time-consuming method compared with the denuder method because longer weighing intervals are necessary to get a quantifiable loss of mass when lower output rates are adjusted. Certainly, for the denuder method, an effective coating material towards the target analyte collection is necessary to guarantee the accuracy of output rate measurement. The effect of the length of a smaller capillary (0.10 mm i.d.) on the test gas output of ICl is shown in Fig. 2B. As before, the output rate decreases with an increase of capillary length. The data obtained by the gravimetric method and denuder method were again very similar when a capillary length of 2.5 cm was used, however, with the increase of the capillary length significant differences (7.6–17.9%) were observed between these two sets of data (Fig. 2B). Furthermore, in such cases, the precisions of the gas sources (RSD (relative standard deviation) = 6.0–13.5%) were worse than the data obtained by using 0.53 mm i.d. capillaries (RSD = 3.6–7.1%). These results indicate that the test gas source might be more and more unstable when smaller and longer capillaries (0.10 mm i.d. × length 5–20 cm) are used for the generation of highly volatile gases, such as ICl. Actually, one major problem using smaller capillaries was the formation of liquid droplets of ICl inside the diffusion capillary tube (0.10 mm i.d. × length 5–20 cm), which certainly affects dramatically the output rate and the stability of the gas source [10].

## 4. Conclusions

This paper shows that capillary diffusion devices are an effective approach for the generation of gaseous standards of halogens. However, the experimental output rate matches the theoretical prediction only if a capillary with relatively large dimension (>1–2 mm i.d.) is applied. When a capillary with smaller dimension is used, the actual test gas output can be elevated by up to two orders of magnitude compared to their respective theoretical values. Moreover, relatively poor reproducibility is observed for the standard gas source when capillaries with small inner diameter and larger length are used (i.e. 0.10 mm i.d. × length 5–20 cm). In addition, the paper demonstrates that a suitable diffusion denuder method to measure the test gas output can be beneficial, since it is less time-consuming than the gravimetric method.

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