

Atmospheric CFC-11 and CCl₄: A free calibration standard for PTR-MS

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ABSTRACT

Proton-transfer-reaction mass spectrometry (PTR-MS) is an analytical technique used to monitor volatile organic compounds in real-time. For quantitative analysis, compounds of interest are typically calibrated using gas standards, but PTR-MS is quantitative to uncalibrated compounds if the mass-dependent transmission is well defined. However, long-term measurements are challenging due to the drift in transmission over time. Performing frequent calibrations helps, but the methods are time-consuming and tedious, often leading to instruments being under-calibrated. Here we show the use of long-lived and globally monitored compounds in the atmosphere as a tool to constrain the transmission between calibrations. The major ion of trichlorofluoromethane (CFC-11) and carbon tetrachloride (CCl₄) is found at the mass-to-charge ratio (m/z) 116.9, which we propose using to retrieve the transmission of a PTR-MS. We determined the pseudo-reaction rate constants of CFC-11 and CCl₄ to be $0.82 \times 10^{-9} \pm 0.05 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, and $1.65 \times 10^{-9} \pm 0.08 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, respectively. The method introduced here can improve data quality and accuracy, especially for long-term atmospheric measurements.

1. Introduction

Proton-transfer-reaction mass spectrometer (PTR-MS) is an analytical instrument used to monitor volatile organic compounds (VOCs) in real time [1]. It uses gas phase hydronium reagent ions (H₃O⁺) to ionize the analytes, which is considered a soft ionization technique. This results in low fragmentation and enables the detection of organic compounds in relatively complex mixtures [2,3]. Due to this, PTR-MS is used in a variety of applications, including atmospheric chemistry, food science and industry, breath analysis and biogeochemistry [4,5].

PTR-MS is a popular technique because it can measure a wide range of compounds at very high speeds (10 Hz), without any sample treatment. Sub-ppt detection limits can be realized at integration times of a few seconds. Another key advantage is the straightforward proton transfer in the reactor [6], which, in principle allows direct quantification based on simple reaction kinetics. The latter property is not widely exploited because of the poorly constrained mass-dependent transmission of ions through the system in many instruments. In practice, many users use PTR-MS in combination with a gas standard which is used to directly measure the sensitivity (signal per unit concentration) for the compounds of interest [7]. Recently, a dedicated gas standard for PTR-MS was introduced, enabling determination of the transmission up to approximately 400 Th [8]. This constitutes a major step forward to

improve the quantification of uncalibrated compounds.

Despite the progress in determining the transmission of instruments, there are still difficulties with long-term measurements using PTR-MS. This is mainly due to the fact that the transmission drifts over a time-span of days to weeks. Frequent calibrations are therefore necessary to constrain the transmission [5]. In addition, the presence of an internal permeation standard can serve as a tool to observe changes in the transmission. Internal permeation standards are heated chambers which provide a constant supply of a high m/z compound through a membrane. Changes in the intensity of this signal can indicate changes in the transmission. However, this is a relative method because, in practice, it is difficult to determine the absolute amount that is delivered to the instrument.

Here we present the idea of an external calibration standard for PTR-MS using compounds present in the atmosphere. This is an additional tool to increase accuracy and data quality. Any atmospheric compound can be used for calibrating the instrument. The compound must be long-lived, with a stable and known concentration above the limit of detection, and a defined reaction rate with H₃O⁺ in the PTR-MS. One group of compounds which has a potential for this, are chlorofluorocarbons (CFCs). Here, we make use of trichlorofluoromethane (CFC-11) and carbon tetrachloride (CCl₄), which are ozone-depleting substances banned and phased out under the Montreal Protocol in 1987 [9]. The emissions

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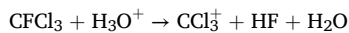
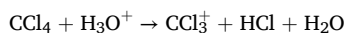
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of CFC-11 and CCl₄ are close to zero, their concentration is closely monitored by several networks [10], and their atmospheric lifetimes are estimated to be 49 years [11], and 32 years [12], respectively. Hence, we can assume that their concentration is known in almost any location in the atmosphere with high accuracy. This makes CFC-11 and CCl₄ suitable as potential calibration compounds for PTR-MS.

In the PTR-MS, trichlorofluoromethane (CFC-11) and carbon tetrachloride (CCl₄) react with hydronium ions to form CCl₃⁺ through the following reactions:



CCl₃⁺ is the only stable ion resulting from these reactions, and its major signal is measured at the mass-to-charge ratio (*m/z*) 116.906 (¹²C³⁵Cl₃⁺), 118.903 (¹²C³⁵Cl₂³⁷Cl⁺), and 120.900 (¹²C³⁵Cl³⁷Cl₂⁺), respectively. CFC-11 and CCl₄ are therefore useable as calibration compounds, but we need to know their proton transfer reaction rates. Previous work has determined the reaction rate constants of H₃O⁺, NO⁺, and O₂⁺ with CCl₄, using selected ion flow tube (SIFT) [13].

This work aims at testing the sensitivity of CFC-11 and CCl₄ in a PTR-MS operated under standard conditions, and to determine the pseudo-reaction rate constants (*k_p*) of CFC-11 and CCl₄ that can be used to constrain the transmission around *m/z* 116.906. This method can be used to improve the accuracy of under-calibrated PTR-MS measurements, or to double check the accuracy of well calibrated PTR-MS studies. An important aspect of the method is that it can be applied to past measurements.

2. Methods

2.1. Preparation of gas standards

Gas mixtures were prepared in two 2.4 L glass bottles using commercial standards of CFC-11 and CCl₄ (2000 µg mL⁻¹ in methanol, Restek, USA), respectively. The bottles were prepared by first evacuating, then filling them with nitrogen gas to remove air and impurities. This was repeated five times before filling the bottles to ambient pressure with nitrogen gas (HiQ Nitrogen 6.0, Linde Gas Benelux, The Netherlands). One bottle was then injected with 4 µL CFC-11-standard, and the other was injected with 4 µL CCl₄-standard, to achieve a final concentration of approx. 500 nmol mol⁻¹.

A reference standard solution of acetone, xylene and trimethylbenzene in methanol was prepared and added to the glass bottles. The reference standard solution was prepared by adding 53, 88 and 100 µL of acetone, xylene and TMB, respectively, into 50 mL of methanol. Four microliters of this solution was added to each of the gas bottles, resulting in the concentrations given in Table 1. The sample preparation steps and analysis were repeated twice. Further information on the chemicals used can be found in Table S1.

2.2. Measurement set-up

The PTR-MS used for measurements was a PTR-TOF4000 with

Table 1

Volume mixing ratios of compounds in sample bottles.

Compound	volume mixing ratio (nmol/mol)	
	Bottle 1	Bottle 2
methanol	9.89 × 10 ⁵	9.89 × 10 ⁵
acetone	575	575
xylene	582	582
TMB	584	584
CFC-11 (bottle 1)	583	–
CCl ₄ (bottle 2)	–	521

hexapole ion optics and ion funnel (Ionicon Analytik GmbH, Austria). The instrument was operated at E/N values of 90 and 120 Td, and a drift tube pressure of 2.95 hPa. Samples were extracted from the sample bottles by filling a 1 mL glass syringe. Using a syringe pump (NE-300, New Era Syringe Pump Systems Inc., USA), they were then injected at a rate of 0.1 mL min⁻¹ into a stream of 113 sccm nitrogen gas. Subsequently the mixture was directed into the heated inlet of the instrument, which was heated to 180 °C. The materials in contact with the sample in the duration between sample preparation and detection were glass, PTFE, and PEEK.

2.3. Calibration procedure

Prior to and post-experiment, the PTR-MS was calibrated using the National Physical Laboratory calibration standard [8] with the calibration gas introduction procedure as described by Holzinger et al. [6]. From the calibration measurements, the transmission of the compounds relative to the transmission of *m/z* 21.0221 was calculated in the software PTRwid [14] and are shown in Table 2. The experiment was repeated twice on May 23, 2023 and June 19, 2023, therefore we show the transmissions from both measurement days.

To estimate the transmission of compounds which are not present in the calibration gas standard, a best-fit transmission curve was calculated using polynomial fit. The fit was forced through the point *p* = [21.0221, 1.0], and the following other *m/z* were used for the fitting:

33.030 (methanol), 42.034 (acetonitrile), 45.033 (acetaldehyde), 59.049 (acetone), 71.048 (methyl vinyl ketone), 73.063 (methyl ethyl ketone), 79.053 (benzene), 93.067 (toluene), 107 (m-xylene), 121 (1,2,4-Trimethyl benzene), 223.067 (D₃-siloxane), 297.081 (D₄-siloxane), 371.102 (D₅-siloxane).

The transmissions used for the polynomial fit are in Table 2, where *m/z* 59.049, 107.083 and 121.099 are measured values and *m/z* 116.906 is the fitted value. The polynomial fit transmission curves are shown as solid lines in Fig. 1.

2.4. Calculating pseudo reaction rate constants (*k_p*)

Pseudo reaction rate constants (*k_p*) of CFC-11 and CCl₄ were calculated from their response and the response of the reference compounds during injection. As explained below, the signals were first corrected for isotopes, then the baseline was subtracted, before the *k_p* was calculated by comparing the signals of CFC-11 and CCl₄ to the reference compounds.

The first step of the calculation involves correcting for isotopic abundance. The signals of acetone (*m/z* 59.049), xylene (*m/z* 107.08), TMB (*m/z* 121.10) and CCl₃⁺ (*m/z* 116.90) were considered for the calculation of the reaction rate constants (Fig. 3). For each compound, only one *m/z* value was used. Each compound was corrected for isotopic abundance, and the ion count rate of the compound, *I_R*, is

$$I_R = I_{RH+(isotope)} * f_{isotope}^{-1} \quad \text{eq. 1}$$

where *I_{RH+(isotope)}* is the ion count rate of the considered (most abundant) isotope. *f_{isotope}* is the fraction of the most abundant isotope relative

Table 2

Transmission of compounds at different E/N values. The transmissions are measured values with the exception of *m/z* 116.906, which is the fitted value.

<i>m/z</i>	Transmission			
	Experiment 1		Experiment 2	
	90 Td	120 Td	90 Td	120 Td
59.049	6.20	7.07	5.89	6.83
107.083	11.0	13.4	10.3	13.0
116.906	11.3	13.6	10.5	13.1
121.099	11.3	13.6	10.5	13.1

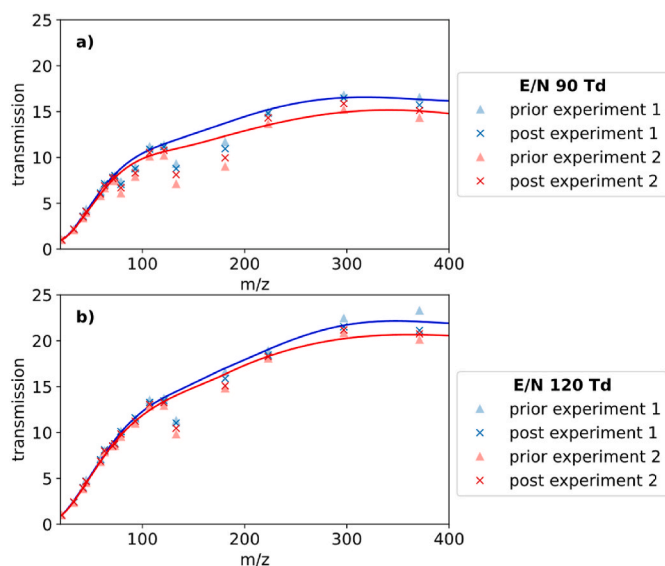


Fig. 1. Transmission curves prior to and post experiments on day 1 and 2 with a) E/N 90 Td and b) E/N 120 Td.

to the sum of all isotopes, which is shown in Table 3 for all ions considered.

An example of the isotope corrected measurement is shown in Fig. 2. Here, we see that xylene and TMB show stickiness evident by their slower increase, and decrease after the injection is done. Acetone and CFC-11 do not stick to the surfaces to the same extent and show faster response times to the start and stop of the sample injection. A section at the end of the measurement where the signals have stabilized was used as the baseline. All other measurements can be found in the supplementary information.

The isotope corrected signals were further processed to remove the baseline signal. First, the ion count signal of each compound was integrated across the whole measurement to determine the total ion counts. Secondly, the baseline area was integrated and then multiplied by the length of the measurement. Finally, the baseline was subtracted from the measurements. The total ion counts (TIC) are calculated by

$$TIC = \int_{t_1}^{t_2} I_R - \frac{t_2 - t_1}{t_4 - t_3} \int_{t_3}^{t_4} I_b \quad \text{eq. 2}$$

where t_1 and t_2 are the start and end of the integration time period, respectively. I_b is the baseline signal of the compound, and t_3 and t_4 are the start and end time of the baseline signal, respectively.

The total ion counts resulting from this was used to determine the pseudo reaction rates of CFC-11 and CCl_4 by comparing their total count rates to the total count rates of acetone, xylene and TMB, respectively. The calculated pseudo reaction rate constants (k_p) were determined by

$$k_p = \frac{TIC_{\text{CFC}}/n_{\text{CFC}}}{TIC_{\text{ref}}/n_{\text{ref}}} \times \frac{T_{\text{ref}}}{T_{m/z \ 116.9}} \times k_{\text{ref}} \quad \text{eq. 3}$$

where n is the number of mols injected, and T is the transmission of the ion determined using the transmission curve, and k_{ref} is the reaction rate constant of the reference compound. The utilized reaction rate constants

Table 3
Isotope corrections factors.

m/z	f_{isotope}
59.049	0.9651
107.08	0.9163
116.90	0.4302
121.10	0.9063

of acetone, xylene and trimethylbenzene are 3.25×10^{-9} , 2.31×10^{-9} , and $2.40 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively [6].

3. Results

Here, we present the k_p of CFC-11 and CCl_4 . The pseudo reaction rate constants were determined by comparing the signals of CFC-11 and CCl_4 to those of acetone, xylene and TMB respectively (equation (3)). A complication that will be discussed below is the uncertainty in the recovery rate of the reference compounds and potentially of CCl_4 and CFC-11.

3.1. Pseudo reaction rate constants of CFC-11 and CCl_4

The calculated k_p of CFC-11 and CCl_4 is based on the assumption that all compounds experience no (or the same) losses when passing through the instrument. However, this might not be the case. As observed in Fig. 2b, xylene and TMB are retained on surfaces and show a slower response time than acetone and CFC-11. We therefore need to investigate how losses of the reference compounds influence the calculated k_p of CFC-11 and CCl_4 .

We quantified the difference between the expected signal and the measured signal of the reference compounds based on the mols injected. This resulted in the recovery rate (RR) of the reference compound, given by

$$RR = \frac{TIC \times V}{t \times n} \frac{1}{S} \times 100\% \quad \text{eq. 4}$$

Where TIC is the total ion counts, V is the total volume of gas in the injection in mols, t is the injection time in seconds, n is the amount of compound injected in nmol, and S is the instrument sensitivity to the compound in cps/ppb (obtained from the calibrations using the NPL gas standard).

The mean recovery rates of acetone, xylene and TMB were $123 \pm 5\%$, $79 \pm 4\%$ and $78 \pm 4\%$ respectively. The calculated reaction rate of CFC-11 and CCl_4 is dependent on the recovery rate of the reference compounds. A plot of the recovery rate of the reference compounds shows how the calculated reaction rate constants are influenced by the recovery rates of the reference compounds (Fig. 3). To compensate for the loss of the reference compounds, the k_p vs. recovery rates is interpolated to a recovery rate of 100 % for the reference compounds. This is simulating no losses or contamination of reference compounds, and results in the best estimation of k_p of CFC-11 and CCl_4 .

The pseudo reaction rate constants of CFC-11 and CCl_4 were determined to be $0.82 \times 10^{-9} \pm 0.05 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, and $1.65 \times 10^{-9} \pm 0.08 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, respectively. The uncertainties are the 95 % confidence interval around the regression at the point where the recovery rate is 100 %.

3.2. How to use k_p for CFC-11 and CCl_4 to calibrate the PTR-MS

The pseudo reaction rates of CFC-11 and CCl_4 can be used to constrain the transmission of a PTR-MS instrument using the measured signal at 116.9 in ambient air. In Fig. 4 we show an example of the signal at m/z 116.9, and its signal in ambient air compared to zero air.

According to de Gouw (2003) the transmission is

$$T(m/z \ 116.9) = \frac{I_{m/z \ 116.9}}{I_{\text{H}_3\text{O}^+} k_p \Delta t [\text{CFC11} + \text{CCl}_4]} * T(m/z \ 21.02) \quad \text{eq. 5}$$

where $[\text{CFC11} + \text{CCl}_4]$ is the combined concentrations of CFC-11 and CCl_4 in the atmosphere, in the unit molecules cm^{-3} . k_p is the pseudo reaction rate constants of CFC-11 and CCl_4 weighted for their relative contribution to the signal at m/z 116.9 (see Table 4). The reaction time, Δt , is given by:

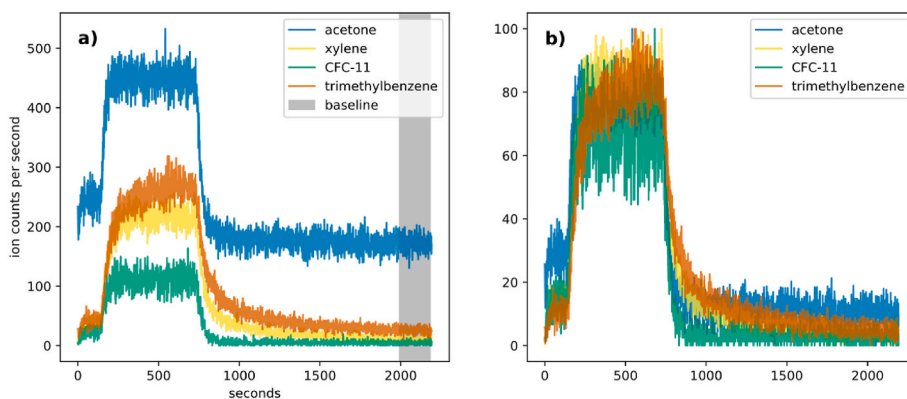


Fig. 2. Instrument response to injection of CFC-11 mixture with acetone, xylene and trimethylbenzene, measured at E/N 90 Td. The syringe was attached to the system at zero seconds and the injection started at 130 s. The shaded area indicates the section used as baseline. **a)** shows isotope corrected signal, and panel **b)** shows normalized response.

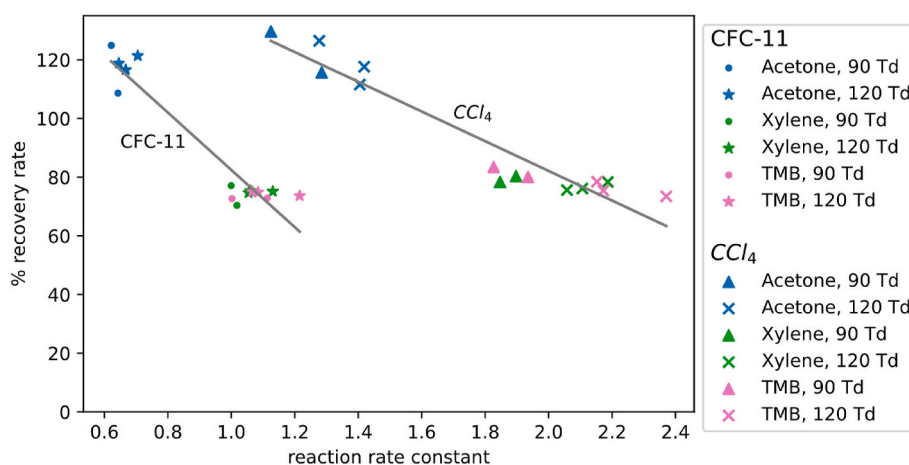


Fig. 3. Recovery rate of acetone, xylene and TMB against calculated reaction rate constant of CFC-11 and CCl_4 .

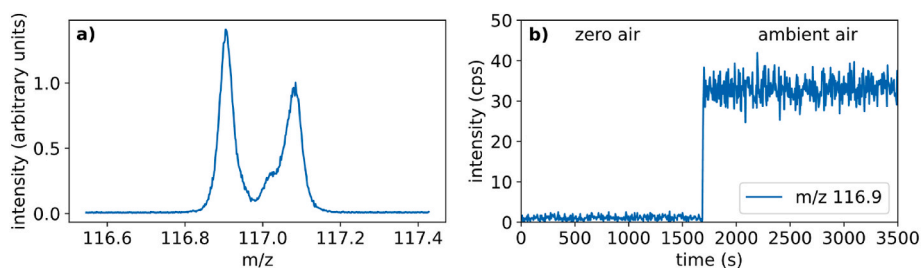


Fig. 4. **a)** mass spectrum of ambient air around m/z 116.9, and **b)** time series of signal at m/z 116.9 in zero air and ambient air.

$$\Delta t = \frac{1}{\mu} \frac{d}{E} = \frac{1}{\mu_0} \frac{pT_0}{p_0T} \frac{d}{E} \quad \text{eq. 6}$$

where d , E , p and T are length, electric field strength, pressure and temperature of the drift tube. T_0 and p_0 are the temperature and pressure at standard conditions (273.15K; 101 325 Pa). μ is the ion mobility of the primary ions, and μ_0 is the reduced ion mobility of the primary ions, which is experimentally determined and has been reported by Dotan et al. [15] for H_3O^+ , $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ in N_2 . We use the μ_0 of the H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, weighted for the abundance of the ions:

$$\text{weighted } \mu_0 = \frac{I_{m/z\ 21} \times 487}{I_{m/z\ 21} \times 487 + I_{m/z\ 39} \times 244} \mu_{\text{H}_3\text{O}^+} + \frac{I_{m/z\ 39} \times 244}{I_{m/z\ 21} \times 487 + I_{m/z\ 39} \times 244} \mu_{\text{H}_3\text{O}^+(\text{H}_2\text{O})} \quad \text{eq. 7}$$

where the $\mu_{\text{H}_3\text{O}^+}$ and $\mu_{\text{H}_3\text{O}^+(\text{H}_2\text{O})}$ used are 2.76 and 2.28 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively.

In addition to the measurements of m/z 116.9, the atmospheric concentration of CFC-11 and CCl_4 is needed to calculate the transmission. Table 4 contains the past and projected global average concentrations of CFC-11 and CCl_4 reported by the World Meteorological Organization [10]. The weighted k_p is calculated and reported. An example calculation from ambient measurements of m/z 116.9 is in the supplementary information. When using other PTR-MS designs where product ions concentrations do not linearly scale with primary ion concentrations, e.g. Vocus IMRs, the signal at m/z 116.9 can be compared to components of a calibration gas standard. Between calibrations, the signal at m/z 116.9 should scale with changes in sensitivity of other ions.

Table 4

Global average concentrations of CFC-11 and CCl₄ and k_p weighted for the concentrations of CFC-11 and CCl₄. The measured and predicted concentrations are reported by WMO [10].

Year	[CFC-11] (ppt)	[CCl ₄] (ppt)	weighted k_p ^b (10^{-9} cm ³ s ⁻¹ molecule ⁻¹)
2000	259.9	98.6	1.05
2005	250.4	93.7	1.05
2010	240.4	87.9	1.04
2015	231.6	82.4	1.04
2020	225.0	77.3	1.03
2025 ^a	215.8	72.5	1.03
2030 ^a	205.3	65.6	1.02

^a predicted concentrations.

$$^b \text{weighted } k_p = \frac{[\text{CFC11}]}{[\text{CFC11}] + [\text{CCl}_4]} k_{p(\text{CFC11})} + \frac{[\text{CCl}_4]}{[\text{CFC11}] + [\text{CCl}_4]} k_{p(\text{CCl}_4)}$$

4. Discussion

The determination of the k_p is based on the assumption that no CFC-11 and CCl₄ is lost in the system, while we account for the recovery of acetone, xylene and TMB. Xylene and TMB show that they stick to surfaces through to their slower response to the injection (Fig. 3). This is also indicated by the lower recovery rates of xylene and TMB, at 76 ± 3 % and 76 ± 3 % respectively. We do not observe the same stickiness from acetone, CFC-11 or CCl₄. We therefore do not expect significant losses of these compounds. On the contrary, the recovery rate of acetone exceeds 100 %. This can either be explained by contamination, uncertainty in the preparation of the standard, or uncertainties in the calibration gas standard used to determine the sensitivities. To determine if the excess acetone signal was caused by contamination in the sample preparation and measurements, we performed the experiment without acetone added. No excess signal was observed at m/z 59, meaning the high levels of acetone are not explained by contamination. Another explanation for this could be the error involved with pipetting volatile liquids. We evaluated the pipetting technique and found a 4 % error in the volume, thus this does not account for all of the excess acetone observed. We therefore conclude that the acetone recovery rate of 119 ± 6 % may also reflect uncertainty in the calibration set-up. The uncertainty in the standard itself is within 5 % for acetone, and within 3 % for xylene and TMB [8]. The recovery rates of acetone, xylene and TMB are accounted for, hence we do not expect the deviation from 100 % recovery to affect the calculated reaction rates of CFC-11 and CCl₄. Our determined CCl₄ reaction rate of $1.65 \pm 0.08 \times 10^{-9}$ cm³ s⁻¹ molecule⁻¹ matches well the CCl₄ reaction rate determined using selective ion flow tube, which is reported to be 1.7×10^{-9} cm³ s⁻¹ molecule⁻¹ [13].

The method of using CFC-11 and CCl₄ to assess the transmission of a PTR-MS is dependent on accurate measurements of CFC-11 and CCl₄ concentrations in the atmosphere. Global monitoring networks such as Advanced Global Atmospheric Gases Experiment (AGAGE) measure in-situ and flask samples on an hourly to weekly basis. While studies have demonstrated that atmospheric background measurements of CFC-11 closely match measurements done by the AGAGE [16], regional differences can occur compared to global averages. This is due to differences in regional emissions and meteorological conditions, which can contribute to variation in the atmospheric CFC-11 concentration up to 14.4 % (relative standard deviation) [17]. However, since the discovery of unreported emissions of CFC-11 around 2012, there has been a decrease in these emissions [18,19]. Currently, we therefore expect the regional deviations from average concentrations of CFC-11 and CCl₄ to be minor, although some variations can occur and must be taken into consideration.

Using CFC-11 and CCl₄ as a tool to retrieve the transmission can be a valuable addition to atmospheric measurement campaigns using PTR-MS, and has several advantages. The transmission of instruments tends to drift over time, so implementing this tool can increase the accuracy of

quantification and data quality. The advantage of this method is that it provides a completely independent quality control tool when added to laboratory and field calibrations. However, calibrations should remain the backbone of quantitative PTR-MS measurements. Another advantage of this tool is that no separate measurements are needed to use the presented method, which is very useful for long-term campaigns. This method also allows for checking data quality for past campaigns. Additionally, many interesting compounds have a similar m/z value to m/z 116.9 and for most instruments this section of the transmission curve is not steep. This constitutes that m/z 116.9 is a useful tool for checking the general stability of the instrument. Previous work determined that CCl₄ also reacts with NO⁺ and O₂⁺ to form CCl₃⁺ [13]. This suggests that this method could be used with other ion chemistries, provided the respective reaction constants are determined. In addition, other CFCs at different m/z might be possible to add to this procedure, provided they have a high enough concentration to be detected, and their reaction rate is sufficiently high.

5. Conclusion

Here we report the reaction rate constants of CFC-11 and CCl₄ in PTR-MS. The pseudo reaction rates of CFC-11 and CCl₄ were found to be $0.82 \times 10^{-9} \pm 0.05 \times 10^{-9}$ cm³ s⁻¹ molecule⁻¹, and $1.65 \times 10^{-9} \pm 0.08 \times 10^{-9}$ cm³ s⁻¹ molecule⁻¹, respectively. We propose the use of the signal at m/z 116.9 to retrieve the transmission of a PTR-MS, which has the advantage of being present in all ambient measurements.

CFC-11 and CCl₄ concentrations are measured through a wide global monitoring network, and their future concentrations are predicted [10]. We proposed adding the signal at m/z 116.9 to measurement and data processing procedures, allowing the transmission to be retrieved during atmospheric measurements, and between calibrations using calibration standards. This tool provides an insight into instrument stability, can improve data quality and accuracy, and is especially useful for long-term atmospheric measurements using PTR-MS.

CRedit authorship contribution statement

Hanne Ødegaard Notø: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis. **Rupert Holzinger:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

I uploaded the data used in the processing to a repository and it is available for download here: <https://doi.org/10.5281/zenodo.13136243>

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijms.2024.117311>

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