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Short communication

Corrected equation for the concentrations in the drift tube of a proton transfer reaction-mass spectrometer (PTR-MS)

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Abstract

A corrected equation for the concentrations in the drift tube of a proton transfer reaction-mass spectrometer (PTR-MS) is presented which accounts for the different mobility of primary ions and protonated analyte volatile organic compounds (VOCs). As a consequence, the calculation of VOC concentrations from the measured count rates requires as well a correction factor, equalling the ratio of (i) the mobility of the protonated analyte VOCs to (ii) the mobility of the gases used to determine the transmission efficiency. However, such data do essentially not exist for the relevant VOCs. Published mobility data for small inorganic ions suggest that the correction can be larger than 20% and hence be a significant contribution to the overall accuracy of calculated concentrations. The correction emphasises the need to calibrate the PTR-MS in order to determine VOC concentrations accurately.

Keywords: Proton transfer reaction-mass spectrometry; Volatile organic compounds

1. Introduction

A proton transfer reaction-mass spectrometer (PTR-MS) is a compact and affordable device that enables measurements of many volatile organic compounds (VOCs) with high sensitivity and short response time. Moreover, it is essentially a real time instrument and does not require any sample treatment. Due to these advantages, PTR-MS is nowadays frequently applied in environmental measurements, breath gas analysis and food chemistry. Configuration, function and application of a PTR-MS have been described in detail [1–3] and a sketch of the PTR-MS is shown in Fig. 1. The ion source generates hydronium primary ions which pour into the drift tube. The drift tube, featuring a length of ∼10 cm and a diameter of ∼2 cm, consists of a number of segments in order to establish a homogeneous electric field E parallel to the drift tube axis. This field is applied in order to enhance the kinetic energy of the ions and thus to prevent the substantial formation of cluster ions and to ease the interpretation of the mass spectra. The PTR-MS is mostly operated at total voltage across the drift tube of ∼600 V and a pressure inside the tube of ∼2 mbar, corresponding to an E/N (N being the number density of the gas in the drift tube) of ∼120 Td (1 Td = 10^{-17} V cm^2). Due to the field the ions move with a drift velocity v of

$$v = \mu E \tag{1}$$

where μ is the ion mobility. The contribution to the ion velocities from the flow of the sample gas through the drift tube (∼10 cm^3 s^{-1} at STP) is negligible. The reaction time t_R, i.e., the transit time of the primary ions through the drift tube, is around 10^{-4} s. A fraction of primary and product ions is extracted from the drift tube through a small sampling orifice (SO) into an intermediate chamber (IC) where higher collision energies at lower pressure reduce the amount of cluster ions. Then a fraction of the ions enters the nosecone (NC) of the quadrupol mass spectrometer (QMS), and finally the count rates of R_iH^+ and H_3O^+ are measured with a secondary electron multiplier (SEM).

In the drift tube the analyte VOCs of the sample gas, denoted as R_i, are ionized by the proton transfer reaction

$$R_i + H_3O^+ \rightarrow R_iH^+ + H_2O \tag{2}$$

A variety of other processes such as fragmentation [4], electron transfer reactions, formation of clusters, reverse and secondary

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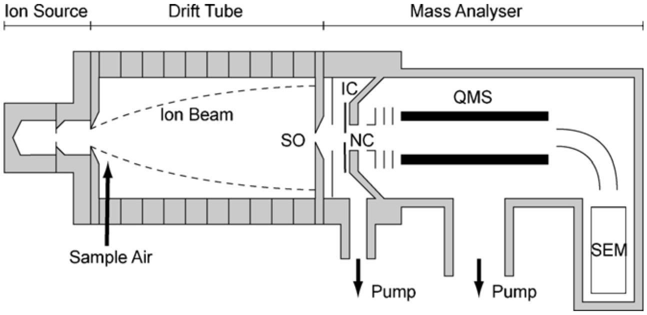

Fig. 1. Schematic of the PTR-MS redrawn from [11]. SO: Sampling orifice; IC: intermediate chamber; NC: nosecone; QMS: quadrupol mass spectrometer, SEM: secondary electron multiplier.

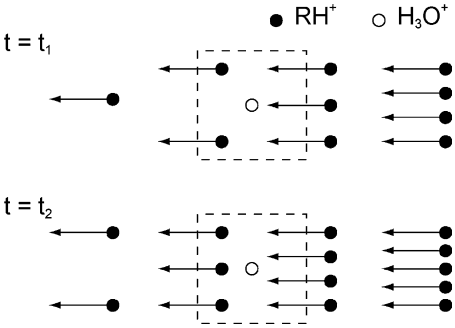

Fig. 2. Illustration of an advection effect for the protonated analyte VOCs in a volume element moving with the velocity of the primary ions.

reactions may also occur and these processes are to be considered for the interpretation of PTR-MS mass spectra. The reactions are particularly complex for humid samples where the VOCs react not only with the primary ions, but to a large extent also with water clusters, either by proton transfer or by switching reactions. Also secondary reactions between the product ions and neutral water molecules are important for humid samples. However, as for the pure the proton transfer reaction (2), the established relation between the concentrations of primary ions, non-protonated and protonated VOCs at the end of the drift tube is [1–3]

$$[R_i] = \frac{[R_i\mathrm{H}^+]}{k_i t_\mathrm{R}[\mathrm{H_3O^+}]} \tag{3}$$

where k_i is the reaction rate constant for molecule R_i. Eq. (2) was frequently used for the interpretation of PTR-MS signals and particularly for calculating VOC concentrations in the sample [2,3,5–8] with the only additional requirement that the transmission efficiency of the mass spectrometer must be determined.

The derivation of Eq. (3), however, is obviously based on the assumption

$$\frac{\partial[\mathrm{H_3O^+}]}{\partial t} = -\sum_i \frac{\partial[R_i\mathrm{H}^+]}{\partial t} \tag{4}$$

where the concentrations apparently refer to a volume element which is moving through the drift tube with the speed of the primary ions. Eq. (4) would be correct if the concentrations in such a volume element were changed only by the reaction (2). Such an assumption is appropriate, e.g., for the flow tube of a selected ion flow tube-mass spectrometer (SIFT-MS) where all ions types have essentially the same velocity [9]. However for the PTR-MS, the velocity of the $R_i\mathrm{H}^+$ ions can be much lower than the velocity of the $\mathrm{H_3O^+}$ ions since the former feature usually a larger *m/z* and a lower mobility, with an example shown below. Thus, in this moving volume element, there is obviously a flux of $R_i\mathrm{H}^+$ ions into the right face and out of the left face as illustrated in Fig. 2. Since the $R_i\mathrm{H}^+$ concentrations are increasing between ion source and sampling orifice, this causes a positive net flux of $R_i\mathrm{H}^+$ ions into the volume element, a contribution that we may call “advection”, although it is not advection in the sense that impurities are transported with the flow of the sample gas in the drift tube. Consequently, the increase of $\sum_i[R_i\mathrm{H}^+]$ as a function of time is actually higher than the decrease of $[\mathrm{H_3O^+}]$ and Eqs. (3) and (4) are evidently not in agreement with the transport equation.

Here we present the corrected version of Eq. (3) and discuss the implications for the interpretation of PTR-MS count rates.

2. Concentrations in the drift tube

To derive a corrected equation for the concentrations in the drift tube we prefer to use a one-dimensional coordinate system fixed to the axis of the drift tube cylinder, $x = 0$ corresponds to the inlet from the ion source and $x = L$ to the sampling orifice. No moving volume elements are considered. Then the ion concentrations are determined by the transport equation:

$$\frac{\partial[\mathrm{H_3O^+}]}{\partial t} = -\frac{\partial(v_\mathrm{H_3O}[\mathrm{H_3O^+}])}{\partial x} - \sum_i k_i[R_i][\mathrm{H_3O^+}] \tag{5}$$

$$\frac{\partial[R_i\mathrm{H}^+]}{\partial t} = -\frac{\partial(v_{R_i\mathrm{H}}[R_i\mathrm{H}^+])}{\partial x} + k_i[R_i][\mathrm{H_3O^+}] \tag{6}$$

where in each case the first term on the right side represents advection. The stationary solution of Eq. (5) is, since $[R_i]$ is homogeneous:

$$[\mathrm{H_3O^+}] = [\mathrm{H_3O^+}]_0 \exp\left(-\frac{\sum_i k_i[R_i]}{v_\mathrm{H_3O}}x\right) \tag{7}$$

with $[\mathrm{A}]_0$ or $[\mathrm{A}]_L$ denoting the concentration of component A at position $x = 0$ and $x = L$, respectively. Using Eq. (7), a stationary solution of Eq. (6) is:

$$\frac{\partial[R_i\mathrm{H}^+]}{\partial x} = \frac{k_i}{v_{R_i\mathrm{H}}}[R_i][\mathrm{H_3O^+}]_0 \exp\left(-\frac{\sum_j k_j[R_j]}{v_\mathrm{H_3O}}x\right) \tag{8}$$

Solution for (8):

$$[R_i\mathrm{H}^+] = \frac{k_i[R_i]}{\sum_j k_j[R_j]}\frac{v_\mathrm{H_3O}}{v_{R_i\mathrm{H}}}[\mathrm{H_3O^+}]_0 \times \left(1 - \exp\left(-\frac{\sum_j k_j[R_j]}{v_\mathrm{H_3O}}x\right)\right) \tag{9}$$

With some further mathematical steps we get finally:

$$[R_i] = \frac{[R_i\text{H}^+]_L}{k_i t_R [\text{H}_3\text{O}^+]_L} \frac{\mu_{R_i\text{H}}}{\mu_{\text{H}_3\text{O}}} \tag{10}$$

Hence, the established relation, Eq. (3), is modified by a correction factor equalling the ratio of mobility of the $R_i\text{H}^+$ and of H_3O^+. Measured reduced mobilities in nitrogen at 120 Td and 298 K [10] may serve as an illustration of potential numerical values of the ratio. The values for H_3O^+ and N_2H^+ are 2.81 and 2.05 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$, respectively, and hence the correction factor changes the calculated trace gas concentrations by 37%. Since the mobility tends to be lower for ions with high *m/z*, a larger correction can be expected for heavy VOCs.

Eq. (3) disregards not only advection as discussed above but also diffusion, and particularly diffusion transverse to the drift tube axis can be suspected to lower the concentrations near the sampling orifice. It was claimed that the decrease is usually small for the primary ions [11], however, that does not imply that the relevant quantity, i.e., the ratio $[R_i\text{H}^+]/[\text{H}_3\text{O}^+]$ near the sampling orifice, is unaffected by diffusion. To discuss this issue we may consider the root-mean-square displacement (RMSD) of a one-dimensional δ-function after being subject to diffusion for the residence time in the drift tube t_{res},

$$\text{RMSD} = \sqrt{2Dt_{\text{res}}} \tag{11}$$

with D being the transverse diffusion coefficient of the ion. If all ions have the same velocity and thus the same residence time, the RMSD is larger for ions of lower mass which feature usually a higher diffusion coefficient. Hence, light primary ions diffuse faster towards the walls of the flow tube than heavier product ions and thus the ratio $[R_i\text{H}^+]/[\text{H}_3\text{O}^+]$ increases. For SIFT-MS, this differential diffusion is a well-known effect and a correction factor has been established [12]. For the PTR-MS, however, t_{res} is not constant but inversely proportional to the ion mobility and hence the RMSD is controlled by the ratio D/μ. At vanishingly small electric fields the ratio D/μ is, according to the Einstein relation, identical for all ions. Hence, the relative decrease of concentrations should be similar for all ions and the ratio $[R_i\text{H}^+]/[\text{H}_3\text{O}^+]$ not be affected by diffusion. However, the drift tube of a PTR-MS is not operated at vanishingly electric field but rather at *E/N* of ∼120 Td. At such conditions the ratio D/μ can be much higher than at 0 Td and the increase is quite different for different ions. To give some examples, the increase of D/μ between 0 and 120 Td amounts to a factor of 3.4 for N^+ in N_2, 3.6 for $^7\text{Li}^+$ in N_2, 2 for He^+ in He, but 35 for Li^+ in He [13,14]. For the ions relevant for the PTR-MS analyses the ratios D/μ at 120 Td have not been measured but similar differences might be expected. Hence, an effect of transverse diffusion on the ratio $[R_i\text{H}^+]/[\text{H}_3\text{O}^+]$ in the drift tube of a PTR-MS cannot generally be excluded. The quantification, however, would require (i) to measure or calculate the ratios D/μ at drift tube conditions, and (ii) to derive a correction factor similar to the flow tubes of a SIFT-MS [12] but with the transport kinetics adapted to the drift tube of the PTR-MS.

3. Measured count rates

As for PTR-MS measurements, it is commonly assumed that the measured count rate or current at the mass of the ion A^+, I_A, is proportional to the densities of the ions near the sampling orifice

$$I_\text{A} = T_\text{A}[\text{A}^+]_\text{L} \tag{12}$$

Following a recent review [11], T_A is referred to as the transmission efficiency for the ion A^+. However, different terms are in use, T_A was previously sometimes called “transmission” [6] and the ratio of transmission efficiencies of product ions to transmission efficiency of primary ions is sometimes termed “mass discrimination factor”. This transmission efficiency includes the transfer of ions from the drift tube into the QMS, the transmission efficiency of the QMS and the detection efficiency of the SEM. Note that Eq. (12) implies, if T_A is as usually assumed only a function of *m/z*, that the measured current is independent of the drift velocity at a given number concentration. Due to ion optical discrimination, the electric field applied to the downstream side of the sampling orifice or hydrodynamic effects that will might be the case but it should be confirmed experimentally. Potentially a definition of the transmission efficiency which involves the ion flux or current density near the end of the drift tube could be more appropriate.

To calculate concentrations using Eq. (10) there is the need to measure the ratio of transmission efficiencies of H_3O^+ and $R_i\text{H}^+$, $T_{\text{H}_3\text{O}}/T_{R_i\text{H}}$. The standard method to determine this ratio is using a sample containing a single trace gas R_k in high concentrations so that a clear decrease of the primary signal is observed. By combining Eqs. (7) and (9) and the accepted definition (12), the required ratio of transmissions turns out to be

$$\frac{T_{\text{H}_3\text{O}}}{T_{R_k\text{H}}} = -\frac{\mu_{\text{H}_3\text{O}}}{\mu_{R_k\text{H}}} \frac{\partial I_{\text{H}_3\text{O}}}{\partial I_{R_k\text{H}}} \tag{13}$$

Due to the correction factor in Eq. (10) a ratio of mobilities must now also be considered when determining the ratio of transmission efficiencies. The ratio is usually measured for several different substances R_k covering the desired mass range, and then an interpolated function of *m/z* is used. However, for our discussion we focus on the case that R_k and R_i have the same *m/z*, i.e., the measured ratio of transmission efficiencies is used to determine the concentrations of a molecule R_i with the same *m/z*. Then the concentrations are

$$[R_i] = \frac{1}{k_i t_\text{R}} \frac{\mu_{R_i\text{H}}}{\mu_{R_k\text{H}}} \frac{I_{R_i\text{H}}}{I_{\text{H}_3\text{O}}} \left(-\frac{\partial I_{\text{H}_3\text{O}}}{\partial I_{R_k\text{H}}}\right) \tag{14}$$

which is the established equation

$$[R_i] = \frac{1}{k_i t_\text{R}} \frac{I_{R_i\text{H}}}{I_{\text{H}_3\text{O}}} \left(-\frac{\partial I_{\text{H}_3\text{O}}}{\partial I_{R_k\text{H}}}\right) \tag{15}$$

modified by a correction factor equalling the ratio of mobility of protonated analyte, $R_i\text{H}^+$, and the protonated gas used for determining the ratio of transmission, $R_k\text{H}^+$.

4. Discussion

The correction factor derived above equals unity if $R_i = R_k$ and it can be suspected that an experiment which demonstrated the strong potential of the PTR-MS for quantitatively measuring concentrations [15] was done for this special case. For the general case $R_i \neq R_k$ the correction factor will differ from unity and the potential differences can be estimated from the data for mobilities of light inorganic ions in air at 120 Td [16]. For example, the reduced mobility is 3.2 cm^2 V^{-1} s^{-1} for NO$^+$ ($m/z = 30$) and 2.6 cm^2 V^{-1} s^{-1} for O$_2$$^+$ ($m/z = 32$), indicating that the ratio of mobilities, even for ions of nearly the same mass, can differ from unity by more than 20%. Besides, different mobilities for isobaric ions were already used in the PTR-MS measurements to identify the ions by measuring their arrival time spectrum [1]. Again, much larger differences can be expected for heavier molecules since the correlation of mobility and mass decreases with m/z [16]. This uncertainty of more than 20% due to the correction factor might be compared with the accuracy of the others quantities in the established relation (15).

The accuracy of measured reaction rate coefficients [17–20] is specified to 20–30%. However, for exothermic proton transfer reactions the measured reaction rate coefficient is in excellent agreement with the collision rate coefficient calculated by Langevin theory, suggesting that the accuracy of the measured values is actually probably better than 10%. These reaction rate coefficients are measured using the SIFT-MS or the flowing afterglow techniques at thermal energy, i.e., at a mean relative center-of-mass kinetic energy of the reacting ion-neutral pair KE_{CM} of ~0.025 eV. However, for the PTR-MS an additional uncertainty arises since the reactions in the drift tube occur at ~120 Td corresponding to $KE_{CM} = \sim 0.3$ eV. For nonpolar compounds, k is independent of KE_{CM} and hence the thermal energy values can be applied to PTR-MS analysis. For polar compounds, however, k decreases with increasing KE_{CM} [21] and to my knowledge there are no published data for drift tube conditions.

The accuracy reaction time t_R is estimated to 10% [22] at dry conditions. For humid samples t_R is less accurate because the analyte VOCs react not only with the primary ions but also with water clusters. The accuracy of the measured ratio of changes of count rates for the transmission efficiencies should be better than 10%.

Accordingly, the combined accuracy in Eq. (15) is 15–20% for the ideal case that a nonpolar molecule is measured at dry conditions and here the correction factor due to the ion mobility of 20% contributes significantly to overall accuracy. The correction is less important for typical measurements where the accuracy might be rather 30–50%.

5. Conclusions

The accuracy of VOC concentrations calculated from PTR-MS count rates suffers not only from the errors of reaction rate coefficients, transmission efficiency and reaction time, but also from uncertainties due to an unknown ratio of mobilities and potentially from an effect of transverse diffusion. These uncertainties could significantly contribute to the deviations between concentrations calculated from the count rates and the reference value of gas standards [23]. The uncertainties emphasise the strong need to calibrate the PTR-MS if reliable VOC concentrations are desired as it has been realised by many users [11,24].

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