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PROTON TRANSFER REACTION MASS SPECTROMETRY (PTR-MS)

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28.1 INTRODUCTION

Proton transfer reaction mass spectrometry (PTR-MS) was first developed at the Institute of Ion Physics of Innsbruck University in the 1990s. Nowadays, PTR-MS is a well-developed and commercially available technique for the on-line monitoring of trace volatile organic compounds (VOCs) down to parts per trillion by volume (ppt) level. PTR-MS has some advantages such as rapid response, soft chemical ionization (CI), absolute quantification, and high sensitivity. In general, a standard PTR-MS instrument consists of external ion source, drift tube, and mass analysis detection system. Figure 28.1 illustrates the basic composition of the PTR-MS instrument constructed in our laboratory using a quadrupole mass spectrometer as the detection system.

28.1.1 Ion Source

Perhaps the most remarkable feature of PTR-MS is the special CI mode through well-controlled proton transfer reaction, in which the neutral molecule M may be converted to a nearly unique protonated molecular ion MH^+. This ionization mode is completely different from traditional mass spectrometry (MS) where electron impact (EI) with energy of 70 eV is often used to ionize chemicals like VOCs. Although the EI source has been widely used with the commercial MS instruments most coupled with a variety of chromatography techniques, these MS platforms have a major deficiency: in the course of ionization, the molecule will be dissociated to many fragment ions. This extensive fragmentation may result in complex mass spectra especially when a mixture is measured. If a chromatographic separation method is not used prior to MS, then the resulting mass spectra from EI may be so complicated that identification and quantification of the compounds can be very difficult. In PTR-MS instrument, the hollow cathode discharge is served as a typical ion source [1], although plane electrode direct current discharge [2] and radioactive ionization sources [3] recently have been reported. All of the ion sources are used to generate clean and intense primary reagent ions like H_3O^+. Water vapor is a regular gas in the hollow cathode discharge where H_2O molecule can be ionized according to the following ways [4]:

$$e + H_2O \rightarrow H_2^+ + O + 2e, \quad (28.1)$$

$$e + H_2O \rightarrow H^+ + OH + 2e, \quad (28.2)$$

$$e + H_2O \rightarrow O^+ + H_2 + 2e, \quad (28.3)$$

$$e + H_2O \rightarrow H_2O^+ + 2e. \quad (28.4)$$

The above ions are injected into a short source drift region and further react with H_2O ultimately leading to the formation of H_3O^+ via ion–molecule reactions:

$$\begin{aligned} H_2^+ + H_2O &\rightarrow H_2O^+ + H_2 \quad (28.5a) \\ &\rightarrow H_3O^+ + H \quad (28.5b) \end{aligned}$$

$$H^+ + H_2O \rightarrow H_2O^+ + H \quad (28.6)$$

$$O^+ + H_2O \rightarrow H_2O^+ + O \quad (28.7)$$

$$\begin{aligned} OH^+ + H_2O &\rightarrow H_3O^+ + O \quad (28.8a) \\ &\rightarrow H_2O^+ + OH \quad (28.8b) \end{aligned}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (28.9)$$

Mass Spectrometry Handbook, First Edition. Edited by Mike S. Lee.

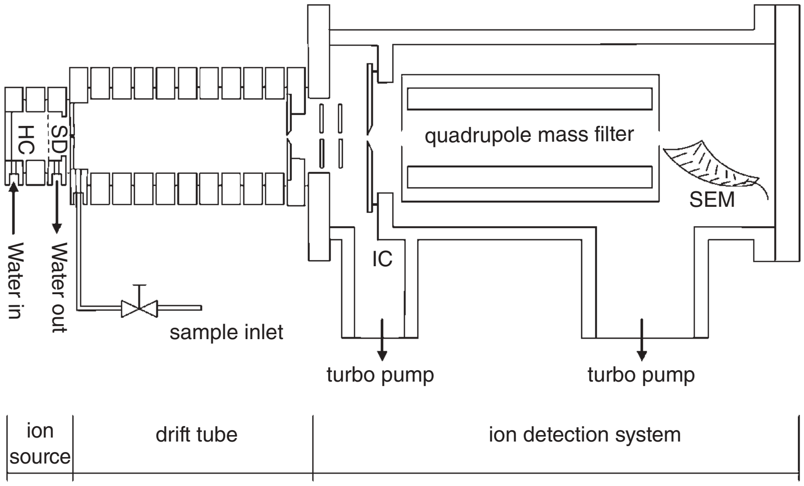


FIGURE 28.1 Schematic diagram of the PTR-MS instrument that contains a hollow cathode (HC), a source drift (SD) region, an intermediate chamber (IC), and a secondary electron multiplier (SEM).

Unfortunately, the water vapor in the source drift region inevitably can form a few of cluster ions $H_3O^+(H_2O)_n$ via the three-body combination process

$$H_3O^+(H_2O)_{n-1} + H_2O + A \rightarrow H_3O^+(H_2O)_n + A \ (n \geq 1), \tag{28.10}$$

where A is a third body. In addition, small amounts of NO^+ and O_2^+ ions occurred due to sample air diffusion into the source region from the downstream drift tube. Thus, an inlet of venturi type has been employed on some PTR-MS systems to prevent air from entering the source drift region [5,6]. At last, the H_3O^+ ions produced in the ion source can have the purity up to >99.5%. Thus, unlike the selected ion flow tube mass spectrometry (SIFT-MS) technique [7], the mass filter for the primary ionic selection is not needed and the H_3O^+ ions can be directly injected into the drift tube. In some PTR-MS, the ion intensity of H_3O^+ is available at 10^6~10^7 counts per second on a mass spectrometer installed in the vacuum chamber at the end of the drift tube. Eventually, the limitation of detection of PTR-MS can reach low ppt level.

Instead of H_3O^+, other primary reagent ions, such as NH_4^+, NO^+, and O_2^+, have been investigated in PTR-MS instrument [8–10]. Because the ion chemistry for these ions is not only proton transfer reaction, the technique is sometimes called CI reaction MS. However, the potential benefits of using these alternative reagents are usually minimal, and to our knowledge, H_3O^+ is still the dominant reagent ion employed in PTR-MS research [1,6,11,12].

28.1.2 Drift Tube

The drift tube consists of a number of metal rings that are equally separated from each other by insulated rings. Between the adjacent metal rings, a series of resistors is connected. A high voltage power supplier produces a voltage gradient and establishes a homogeneous electric field along the axis of the ion reaction drift tube.

The primary H_3O^+ ions are extracted into the ion reaction region and can react with analyte M present in the sample air, which through the inlet is added to the upstream of the ion reaction drift tube. According to the values of proton affinity (PA) (see Table 28.1), the reagent ion H_3O^+ does not react with the main components in air like N_2, O_2, and CO_2. In contrast, the reagent ion can undergo proton transfer reaction with M as long as the PA of M exceeds that of H_2O [6]:

$$M + H_3O^+ \rightarrow MH^+ + H_2O. \tag{28.11}$$

Thus, the ambient air can be directly introduced to achieve an on-line measurement in the PTR-MS operation. Due to the presence of electric field, in the reaction region, the ion energy is closely related to the reduced-field *E/N*, where *E* is the electric field and *N* is the number density of gas in the drift tube. In a typical PTR-MS measurement, *E/N* is required to set to an appropriate value normally in the range of 120~160 Td (1 Td = 10^{-17} Vcm^2/molecule), which may restrain the formation of the water cluster ions $H_3O^+(H_2O)_n$ ($n = 1$–3) to avoid the ligand switch reaction with analyte M [6]:

$$H_3O^+(H_2O)_n + M \rightarrow H_3O^+(H_2O)_{n-1}M + H_2O. \tag{28.12}$$

TABLE 28.1 Proton Affinities of Some Compounds

Compound	Molecular Formula	Molecular Weight	Proton Affinity [13] (kJ/mol)
Helium	He	4	177.8
Neon	Ne	20	198.8
Argon	Ar	40	369.2
Oxygen	O_2	32	421
Nitrogen	N_2	28	493.8
Carbon dioxide	CO_2	44	540.5
Methane	CH_4	16	543.5
Carbon monoxide	CO	28	594
Ethane	C_2H_6	30	596.3
Ethylene	C_2H_4	28	680.5
Water	***H_2O***	***18***	***691***
Hydrogen sulfide	H_2S	34	705
Hydrogen cyanide	HCN	27	712.9
Formic acid	HCOOH	46	742
Benzene	C_6H_6	78	750.4
Propene	C_3H_6	42	751.6
Methanol	CH_3OH	32	754.3
Acetaldehyde	CH_3COH	44	768.5
Ethanol	C_2H_5OH	46	776.4
Acetonitrile	CH_3CN	41	779.2
Acetic acid	CH_3COOH	60	783.7
Toluene	C_7H_8	92	784
Propanal	CH_3CH_2COH	58	786
O-xylene	C_8H_{10}	106	796
Acetone	CH_3COCH_3	58	812
Isoprene	$CH_2C(CH_3)CHCH_2$	68	826.4
Ammonia	NH_3	17	853.6
Aniline	C_6H_7N	93	882.5

However, a higher reduced-field *E/N* can cause the collision-induced dissociation (CID) of the protonated products, thereby complicating the identification of detected analytes.

28.1.3 Mass Analyzer

At the end of the drift tube, there is an intermediate chamber in which most of the air from the drift tube through a small orifice is pumped away. The ions in the drift tube are extracted and focused by the ion optical lens and finally, in a high vacuum chamber, are detected by a quadrupole mass spectrometer with an ion pulse counting system. The ionic count rates $I(H_3O^+)$ and $I(MH^+)$ are measured in counts per second, which are proportional to the respective densities of these ions.

Although quadrupole mass filter is a traditional analyzer in the current PTR-MS instrument, other MS analyzers have been investigated including time-of-flight mass spectrometer (TOF-MS) [14–16], ion trap mass spectrometer (IT-MS) [17], and linear ion trap mass spectrometer (LIT-MS) [18]. These MS techniques have been used to distinguish isomeric/isobaric compounds as discussed in the later section.

28.1.4 Absolute Quantification

Normally, PTR-MS can determine the absolute concentrations of trace VOCs according to well-established ion–molecular reaction kinetics. If trace analyte M reacts with H_3O^+, then the H_3O^+ signal does not decline significantly and can be deemed to be a constant. Thus, the density of product ions $[MH^+]$ at the end of the drift tube is given in Equation 28.13 [6]:

$$[MH^+] = [H_3O^+]_0(1 - e^{-k[M]t}), \qquad (28.13)$$

where $[H_3O^+]_0$ is the density of reagent ions at the end of the drift tube in the absence of analyte M, k is the rate constant of reaction 28.11, and t is the average reaction time the ions spend in the drift tube. In the trace analysis case $k[M]t << 1$, Equation 28.13 can be further deduced to the following form

$$[M] = \frac{[MH^+]}{[H_3O^+]_0}\frac{1}{kt}. \qquad (28.14)$$

Equation 28.14 is often used in a conventional PTR-MS measurement. However, when the concentration of analyte M is rather high, the intensity change of reagent ions H_3O^+ is not neglectable. In this case, the relation $k[M]t << 1$ is not tenable; therefore, the regular Equation 28.14 is no longer suitable for concentration determination. For a more reliable measurement, the following Equation 28.15, deduced from Equation 28.13, can be used to determine the concentration of analyte M. For instance, the concentrations of gaseous cyclohexanone inside the packaging bags of infusion sets were found to be rather high, and its concentrations at several tens of parts per million level could be detected according to Equation 28.15 [19]:

$$[M] = \ln\frac{[H_3O^+]_0}{[H_3O^+]_0 - [MH^+]}\frac{1}{kt}. \qquad (28.15)$$

In PTR-MS instrument, the signal intensities of primary and product ions can be measured. And the reaction time can be derived from the instrument parameters, and the reaction rate constant can be found in literatures for most substances or calculated by the theoretical trajectory model [20,21] using dipole moment and polarizability. Thus, the absolute concentration of trace component can be easily obtained without calibration.

28.1.5 Sensitivity and Limit of Detection

Under the electric field E, the ions in the drift tube move with an average velocity v_{d} given by [22]

$$v_{\mathrm{d}} = \mu \times E, \tag{28.16}$$

where μ is the ion mobility. Generally, the reduced mobility μ_0 is determined as

$$\mu_0 = \left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) \times \mu = \frac{N}{N_0} \times \mu, \tag{28.17}$$

where P is the pressure and T is the temperature in the drift tube. The parameter N_0 is the gas number density at standard pressure p_0 (1 atm) and temperature T_0 (273.15 K). The reaction time t can be calculated from the ion drift velocity (Equation 28.16):

$$t = \frac{L}{v_{\mathrm{d}}} = \frac{L}{\mu_0 N_0} \times \frac{N}{E}, \tag{28.18}$$

where L is the length of the drift tube. Considering the ionic transmission efficiencies of mass analyzer, Equation 28.14 can be expressed as

$$\begin{aligned} \frac{I(\mathrm{MH}^+)}{I(\mathrm{H_3O}^+)_0} &= \frac{[\mathrm{MH}^+]}{[\mathrm{H_3O}^+]_0} \times \tau = [\mathrm{M}]kt\tau \\ &= k\tau[M] \times \left(\frac{L}{\mu_0 N_0} \times \frac{N}{E}\right) \\ &= VMR \times \frac{kL}{\mu_0 N_0} \times \frac{N^2}{E} \times \tau, \end{aligned} \tag{28.19}$$

where the ionic densities $[\mathrm{H_3O^+}]_0$ and $[\mathrm{MH^+}]$ are proportional to the ionic count rate $I(\mathrm{H_3O^+})_0$ and $I(\mathrm{MH^+})$, respectively. The τ is the ionic transmission of $\mathrm{MH^+}$ relative to $\mathrm{H_3O^+}$, and VMR is the volume mixing ratio of trace gas M, $[\mathrm{M}]/N$. The sensitivity is defined as the count rate of $\mathrm{MH^+}$ ions measured at a VMR of 1 ppb and normalized to a condition with $\mathrm{H_3O^+}$ ions of 10^6 cps [23]:

$$\text{Sensitivity} = 10^{-3} \times \frac{kL}{\mu_0 N_0} \times \frac{N^2}{E} \times \tau. \tag{28.20}$$

The sensitivity is expressed in units of normalized ncps/ppb.

The noise statistic (NS) developed from the Poisson distribution has been defined as [24]

$$\mathrm{NS} = \frac{\text{mean signal (cps)}}{\sqrt{\text{mean signal (cps)} \times \text{dwell (s)}}}, \tag{28.21}$$

where the mean signal is the average count rate of many data points for the $\mathrm{MH^+}$ ions at certain dwell time. With PTR-MS, the limit of detection at $\mathrm{MH^+}$ can be obtained at a considered signal-to-noise ratio. From Equations 28.20 to 28.21, the accuracy is limited by the uncertainties in (1) the rate coefficient k, which can be up to 20%–30% [6]; (2) the relative ion transmission τ, which can be specified to 25% [11]; and (3) the reaction time t, which is estimated to 10% [25].

28.2 HOW TO IDENTIFY ISOMERIC/ ISOBARIC COMPOUNDS

In a traditional PTR-MS, the detector is a quadrupole and its mass resolution is rather limited, the ratios of mass to charge (*m/z*) of the product ions cannot be served for a definite indicator of the identity of trace gases because numerous isomeric or isobaric compounds have the same or close molecular weight. In addition, mass overlap from probable fragmentation and cluster ions may be in operation. In particular, when a mixture containing unknown VOC components is investigated, it is inevitable to meet with a question how to identify the compounds.

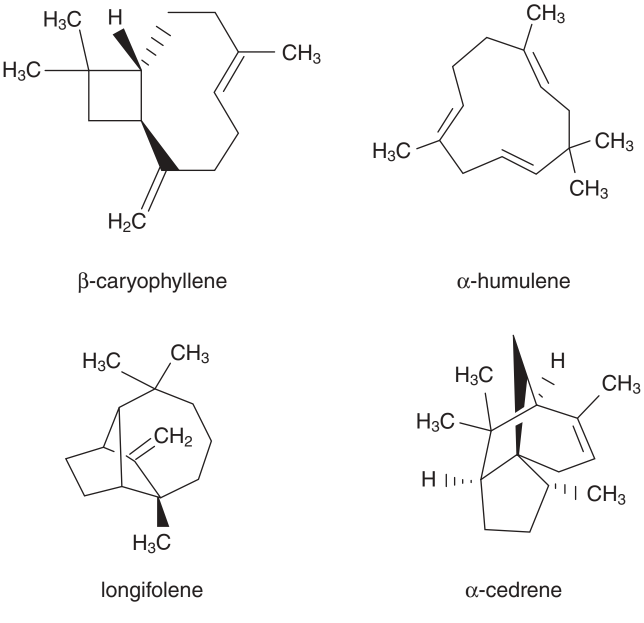
To solve the above problem, different methods have been experimentally attempted, including the change of reduced-field *E/N*, and usage of new reagent ions like $\mathrm{NH_4^+}$, two-stage PTR-MS, PTR-IT (LIT, TOF)-MS, and gas chromatography (GC)-PTR-MS. With these methods, the identification of compounds can be ascertained unambiguously on many occasions. However, it should be noted that the main application of PTR-MS is to monitor VOCs, rather than to analyze compounds, as early claimed by its inventor Lindinger [6].

28.2.1 Changing *E/N*

A variation of reduced-field *E/N* in PTR-MS is quite useful for the identification of compounds, which was first discussed by Hansel et al. [4,6]. An increase in reduced-field *E/N* leads to higher collision energies between the ions and neutral gas molecule in the drift tube and a detailed description about the relationship of reduced-field *E/N* with the ionic kinetic energy was given in a review by Lindinger et al. [6]. When *E/N* increases, due to CID, the ions with the same mass but different intramolecular binding energies exhibit different breakup patterns. Lindinger et al. [6] varied the reduced-field *E/N* by adjusting a voltage between the last two drift rings and the end plate at the end of the drift tube, and found very different breakup efficiency for protonated acetone and propanal both with same *m/z* 59. In the case of the acetic acid and n-propanol, their protonated counterparts both have *m/z* 61, and the fragment ions are also quite different besides distinct breakup efficiency. Different isobars can be identified based on the dissociation dependence of their protonated products on the reduced-field *E/N*.

By varying *E/N* to modulate the hydrated reagent ion distribution, two isobars acrolein (C_3H_4O) and 1-butene (C_4H_8) within a mixture can be resolved and quantitatively determined [26]. In order to better characterize PTR-MS for detection of sesquiterpene released from vegetation, the effects of *E/N* in the range of 80~140 Td on the product ions of β-caryophyllene, α-humulene, α-cedrene, and longifolene have been investigated by Demarcke and coworkers [27]. All sesquiterpenes are isomeric compounds ($C_{15}H_{24}$), and their structures are shown in Figure 28.2.

Our laboratory has also explored changing *E/N* in PTR-MS by a voltage adjustment that crosses the whole drift tube [28]. The product ion distributions were studied for n-propanol/iso-propanol/acetic acid, propanal/acetone, and four isomeric butyl alcohols, and propanal and acetone, with different concentration ratios in three synthetic mixtures, have been differentiated and quantified. In addition, the residual cyclohexanone in a medical device was identified by comparing the reduced-field dependence on product ion distributions between the headspace gas of the infusion sets and the pure cyclohexanone vapor. In practice, one can note that changing *E/N* to identify a compound is not always effective especially for a complex mixture because other protonated compounds can produce the fragmental ions at the same *m/z*.



β-caryophyllene α-humulene

longifolene α-cedrene

FIGURE 28.2 Chemical structures of the four sesquiterpenes. Reprinted with permission from Reference [27]. Copyright 2009 Elsevier.

28.2.2 Using NH_4^+ as Reagent Ions

Aside from H_3O^+, alternative proton donators in PTR-MS have been considered, most notably NH_4^+ [6]. Similarly, NH_4^+ ions can form when NH_3 vapor is used as the discharge gas in the hollow cathode ion source. Proton transfer reaction with NH_4^+ is less exothermic than with H_3O^+ because the PA of NH_3 is higher (162 kJ/mol) than that of H_2O (see Table 28.1). Thus, the NH_4^+ reagent ions might reduce ionic fragmentation and perhaps simplify mass spectral interpretation for those analytes possessing higher PAs than that of NH_3. Of course, one should realize that product ions of the $M{\cdot}NH_4^+$ type likely appear, which are formed by the three-body ion association reaction [9].

Furthermore, if there are two isobaric/isomeric compounds with very different proton affinities and only one of them can accept a proton from NH_4^+, then the two compounds can be unambiguously distinguished from their mixture. An example has been demonstrated by Lindinger and coworkers [6] for a mixture of pinene and 2-ethyl-3,5-dimethylpyrazene, both of them having a molecular mass of 136. Because H_3O^+ may donate a proton to both molecules, it is very difficult to distinguish the two compounds if only H_3O^+ is used as reagent ions. When NH_4^+ was used as the reagent ions, the ionic peak at *m/z* 137 should originate from 2-ethyl-3,5-dimethylpyrazene component. Consequently, the separate PTR-MS experiments using the reagent ions H_3O^+ and NH_4^+ could allow the quantification of pinene and 2-ethyl-3,5-dimethylpyrazene.

The NO^+ ion, an ionic reagent often used in SIFT-MS instrument, is used to distinguish several isobaric aldehydes and ketones. The ionic reaction of NO^+ tends to lead to more fragmentation and the formation of complex that provides a specific mass spectral characteristics to discriminate between aldehyde and ketone molecules [8].

28.2.3 Two-Stage PTR-MS

A two-stage proton transfer reaction ionization to differentiate isomeric compounds with their different PAs has also been investigated [29,30]. In the first stage, proton transfer reaction between H_3O^+ and a selective VOC_1 produces the ions $(VOC_1)H^+$; when a second VOC_2 with a PA larger than that of VOC_1 is present in a sample, a second proton transfer reaction between $(VOC_1)H^+$ and VOC_2 happens to produce the $(VOC_2)H^+$ ions:

$$H_3O^+ + VOC_1 \rightarrow (VOC_1)H^+ + H_2O, \qquad (28.22)$$

$$(VOC_1)H^+ + VOC_2 \rightarrow (VOC_2)H^+ + VOC_1. \qquad (28.23)$$

This method may be useful for distinguishing the isomeric species such as aldehydes and ketones, if appropriate reagent ions are selected. As an example, two isomeric VOCs, having molecular weight 88, ethyl acetate (PA = 836 kJ/mol) and 1,4-dioxane (PA = 798 kJ/mol) were introduced as the samples for VOC_2 and acetone (PA = 812 kJ/mol) was chosen as VOC_1 in the experiment of PTR-TOF-MS [29]. Mass spectra of ethyl acetate and 1,4-dioxane observed in the one-stage and the two-stage are shown in Figure 28.3. These results show that it is possible not only to identify specific molecules, but also to determine their absolute concentrations.

28.2.4 PTR-IT (LIT, TOF)-MS

Although quadrupole dominates in the current PTR-MS instruments, the possibility of utilizing other types of mass analyzers has been investigated, including IT-MS, LIT-MS, and TOF-MS.

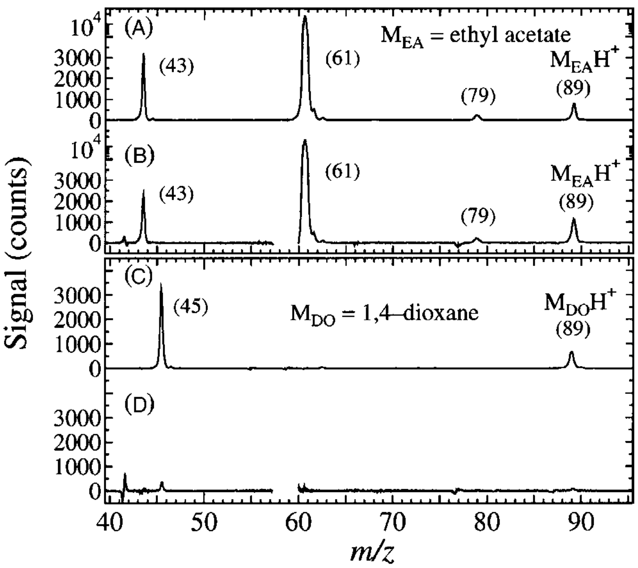


FIGURE 28.3 Mass spectra of ethyl acetate and 1,4-dioxane obtained by the two-stage PTR-MS in the one-stage mode (A) and (C), respectively, and the two-stage mode (B) and (D), respectively. Reprinted with permission from Reference [29]. Copyright 2008 Elsevier.

28.2.4.1 Proton Transfer Reaction Ion Trap Mass Spectrometer (PTR-IT-MS) The IT system used in PTR-MS was firstly reported by Prazeller and coworkers [17], and its cross-sectional view of a prototype instrument is shown in Figure 28.4. The PTR-IT-MS consists of a hollow cathode ion source, a drift tube that

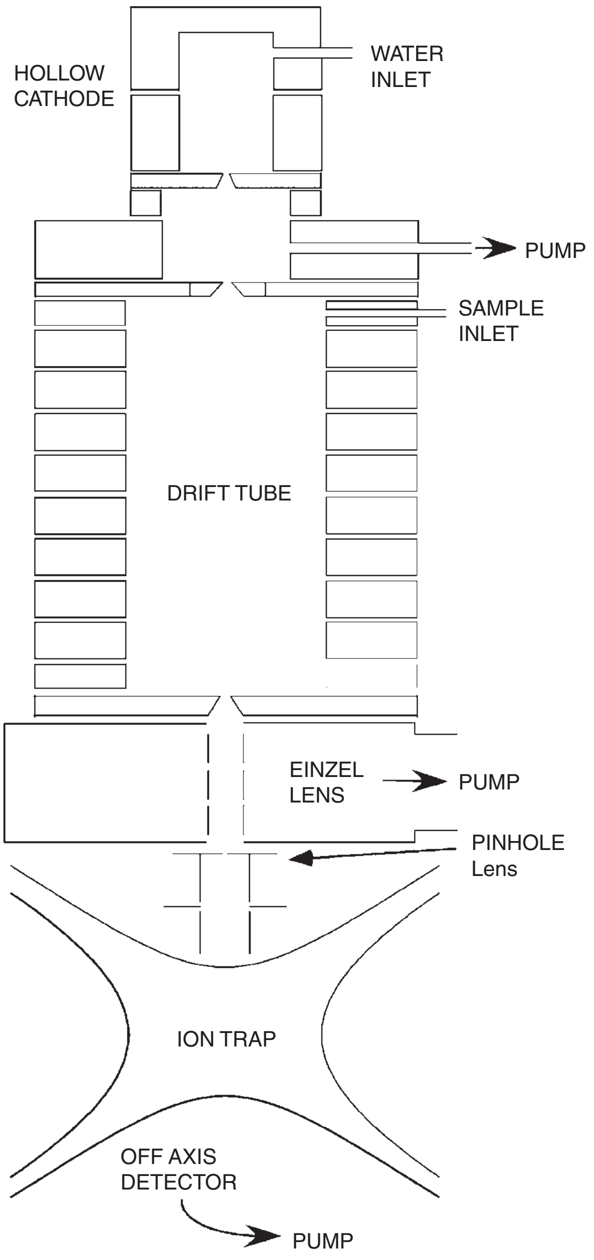


FIGURE 28.4 Schematic diagram of the PTR-IT-MS. Reprinted with permission from Reference [17]. Copyright 2003 Wiley.

is interfaced to a commercial quadrupole IT system via Einzel lens. As opposed to a linear quadrupole mass filter, the PTR-IT-MS instrument has two important potential advantages. The first is a much higher duty cycle at each *m/z* in the mass spectrum deriving from the way that IT mass spectrometry works. In a quadrupole, the duty cycle is given by $t_{\mathrm{dwell}}/[n(t_{\mathrm{dwell}} + t_{\mathrm{shift}})]$, where t_{dwell} is the dwell time at a single mass, t_{shift} is the time required to shift the quadrupole from one *m/z* to the next, and *n* is the number of monitored *m/z*. The more the ions at *m/z* that are to be monitored, the larger the value of *n* and the longer the time it takes to acquire a mass spectrum. However, it is possible to simultaneously store the ions over the entire mass spectrum and scan them out within milliseconds in an IT-MS system. In this case, the duty cycle is a function of the ion storage time (t_{storage}) and the time to scan the ions out of the trap (t_{scan}), which is given by $t_{\mathrm{storage}}/(t_{\mathrm{scan}} + t_{\mathrm{storage}})$. Due to duty cycle higher than quadrupole, IT-MS will have a faster time response in the detection of multiple compounds.

Although CID can be implemented on a standard PTR-MS instrument by elevating the drift tube voltage to increase *E/N*, this approach cannot select a specified *m/z* of interest. As a result, the CID in the drift tube will produce many fragment ions arisen from all the precursor ions present in the drift tube. Unlike the quadrupole MS, the IT-MS has the ability to perform tandem mass spectrometry (MS/MS) studies on mass-selected ions, and thus another advantage of PTR-IT-MS is that isomers/isobars can be distinguished with CID. Meanwhile, in principle, the PTR-IT-MS also has the ability to identify a compound through the specific fragment ions from the CID of the precursor ions. Two pairs of isobaric compounds, methyl vinyl ketone/methacrolein with their ions at *m/z* 71 and acetone/propanal at *m/z* 59, have been distinguished by MS/MS using the CID within the IT of PTR-IT-MS [17].

It is known that monoterpenes may be released from fruits and many plants like pine trees, and they are important in atmospheric chemistry. The CID of 10 isomeric monoterpenes $C_{10}H_{16}$ has been investigated by using a PTR-IT-MS apparatus [31]. The results show that these isomers can be solely identified on the basis of their respective CID patterns. However, PTR-IT-MS is still difficult to distinguish these compounds once several monoterpenes are in a mixture.

28.2.4.2 Proton Transfer Reaction Linear Ion Trap Mass Spectrometer (PTR-LIT-MS) To expand the capacity of PTR-MS to differentiate isobars at ppt level, PTR-LIT-MS has been developed [18], which is similar to the PTR-IT-MS but uses a linear quadrupole IT instead of a hyperbolic IT. In the LIT system, ions are typically trapped radially by an oscillatory quadrupole field and axially with electrostatic barriers provided by two containment lenses. Because the LIT system has a higher ion collection efficiency than that of quadrupole IT, PTR-LIT-MS can be used to detect VOCs at lower concentrations.

Similarly, the isomeric isoprene oxidation products, methyl vinyl ketone and methacrolein, could also be distinguished by adjusting CID voltage in the PTR-LIT-MS. Their limits of detection are about 100 ppt.

28.2.4.3 PTR-TOF-MS An alternative mass analyzer is the TOF-MS. The first PTR-TOF-MS instrument with a radioactive ion source was developed by Blake et al. in 2004 [14]. PTR-TOF-MS instrument with a hollow cathode ion source has been reported [15], and its schematic drawing is shown in Figure 28.5. TOF-MS can simultaneously collect the entire mass spectrum, and consequently, PTR-TOF-MS has a potential for rapid and selective online detection of trace components. In combination with a high-resolution TOF-MS, PTR-TOF-MS can provide more precise molecular weight information, and therefore, isobars can be identified.

28.2.5 GC-PTR-MS

In complex VOC mixtures, some isomeric/isobaric compounds may be present, and there will be some fragment ions that have the same or close ionic masses as other product ions. Under such circumstances, it is almost impossible to identify and quantify every component present using the methods mentioned above. To analyze a complex mixture, one feasible solution is to combine a conventional separation technique GC with PTR-MS. GC-PTR-MS is able to separate and unambiguously identify isomeric/isobaric compounds.

The first GC-PTR-MS experiment was carried out by Fall and coworkers [32], and several subsequent studies were completed by other groups [23,33]. However, the combination of GC with PTR-MS will inevitably result in the loss of real-time detection capability of PTR-MS due to relatively slow preseparation of compounds in a GC column.

28.3 APPLICATIONS

Due to its advantages of rapid response, soft ionization, absolute quantification, and high sensitivity, PTR-MS has been successfully applied to detect VOCs in the environmental fields, including atmospheric monitoring, food research, and water detection [1,6,11,12].

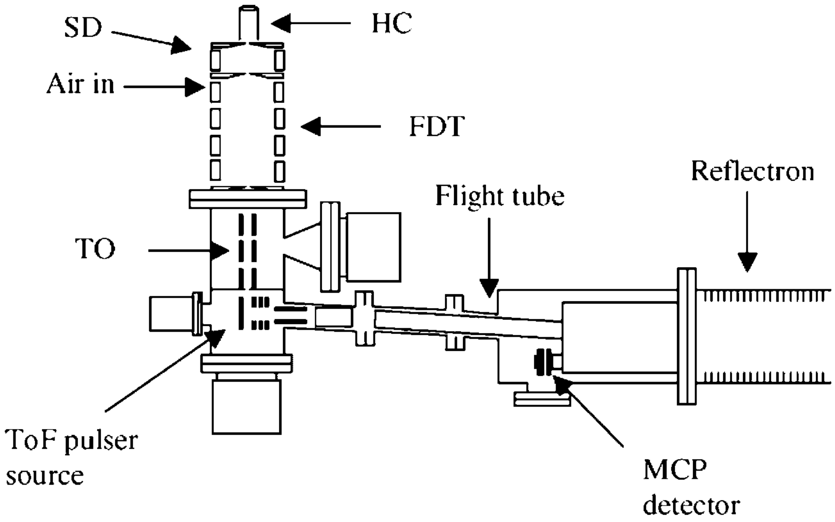


FIGURE 28.5 Schematic drawing of the PTR-TOF-MS system with a hollow cathode ion source. SD, source drift tube; FDT, flow drift tube; TO, transfer optics; MCP, microchannel plate. Reprinted with permission from Reference [15]. Copyright 2005 Elsevier.

28.3.1 Atmospheric Monitoring

The widest application of PTR-MS is in the field of atmospheric monitoring. In air, VOCs originate from diverse sources but primarily from biogenic origin. Many VOCs have effects on the sources and sinks of ozone, aerosol formation, and climate change. In addition, some VOCs are also toxic to human beings [34], so it is important to monitor their concentrations in wider environments. Nowadays, PTR-MS has been used to detect VOCs from plants, forest, and human activities.

28.3.1.1 Plant Emission The annual global natural nonmethane VOC flux that is emitted from living vegetation is estimated to be about 1150 Tg, which is composed of 44% isoprene, 11% monoterpenes, 22.5% other reactive and 22.5% relatively unreactive VOCs [35]. Here, biogenic VOC measurements are emphasized, which are from local plants, wounding leaves, and vegetation over a large regional scale.

Local emissions from specific plants were investigated by Holzinger et al. who have identified methanol, acetaldehyde, ethanol, acetone, acetic acid, isoprene, monoterpenes, toluene, and C_{10}-benzenes emitted from the Mediterranean helm oak (*Quercus ilex* L.) [36]. After flooding, ethanol and acetaldehyde were found to increase, indicating ethanol production under anoxic condition of the root system and the subsequent transport and partial oxidation to acetaldehyde inside the green leaves. Additionally, bursts of acetaldehyde with lower ethanol emission were also found in the case of the fast light/dark changes. The rapid formation of acetaldehyde during light–dark transitions was further investigated with $^{13}CO_2$ labeling experiments, and it was determined that acetaldehyde resulted from a pyruvate overflow mechanism controlled by cytosolic pyruvate levels and pyruvate decarboxylase activity [37]. Similarly, the isotope technique has been used to trace multiple origins of isoprene precursors in leaves [38,39]. It was pointed out that xylem-transported glucose or its degradation products potentially can be used as additional precursors for isoprene biosynthesis and that this carbon source becomes more important under the conditions of limited photosynthesis [38]. The monoterpene concentrations and emission rates from the plants fumigated by methyl salicylate were greater than the same plants controlled at temperatures from 25 to 45°C [40], and the emission rates of isoprene and monoterpenes recovered faster after rewatering the droughted *Q. ilex* seedlings [41]. The effect of flood conditions on the emissions of ethanol, acetaldehyde, and acetic acid in relation to assimilation and transpiration was investigated by PTR-MS and high performance liquid chromatography (HPLC) [42], and the short-chained oxygenated VOC emissions from *Pinus halepensis* saplings were also monitored in response to the changes in water availability, stomatal conductance and transpiration, and light [43].

The emissions of isoprene, acetaldehyde, methanol, and monoterpenes from Sitka spruce correlating with photosynthetic photon flux and temperature have been investigated, and an anticorrelation phenomenon between isoprene and acetaldehyde was reported during the sudden light–dark transitions [44]. Biogenic VOCs from grass crop species, rice, and sorghum widely grown in the southeastern Texas region have also been measured by PTR-MS, PTR-IT-MS, and GC-PTR-MS [45]. And emissions of isoprene, acetaldehyde, monoterpenes, acetone, and ethanol from Norway spruce twigs were best described [46], and these VOC emissions were further monitored in response to temperature changes [47]. The emission rates of monoterpenes, acetone, methanol, hexanal, hexenals, hexanol, and methyl salicylate increased exponentially with temperature. However, the emissions of acetic acid and acetaldehyde rose up to saturation at 30°C, suggesting that the algorithms using only incident irradiance and leaf temperature might be inadequate to predict VOC emission rates. A series of VOCs emitted from *Eucalyptus grandis* leaf at a temperature range of 30~100°C was identified at the optimum drift tube voltages of PTR-MS [48], and isoprene emission from various *Quercus* tree species was studied by PTR-MS and GC-MS. Inversely, the uptake rate of methyl isobutyl ketone by Golden Pothos (*Epipremnum aureum*) was first determined [49], and the formaldehyde emission and uptake by Mediterranean trees *Q. ilex* and *P. halepensis* were also studied [50].

In addition to VOC emissions from normal plants, it is well known that wounding also induces VOC release, and the formation of hexanal and hexenal families in wounding leaves was studied [51]. Another PTR-MS application is to detect VOCs resulting from grazing, herbivory, and other physical damage to plants. Wound-induced VOCs from aspen leaves, beech leaves, and clover were monitored [51]. The rapid emission of (*Z*)-3-hexenal within 1–2 s after wounding leaves and then its disappearance, and the appearance of its metabolites including (*E*)-2-hexenal, hexenols, and hexenyl acetates, are found. The emission of hexenal family compounds was proportional to the extent of wounding, not dependent on light. The effect of oxygen on the formation of hexanal and hexenal family VOCs was also investigated, indicating that there were no large pools of the hexenyl compounds in leaves.

With PTR-MS, high biogenic oxygenated VOCs fluxes were determined with the eddy covariance measurements for about 2 days after hay harvesting, and the dominated compounds were methanol, acetaldehyde, hexenals, and acetone [52]. Eddy covariance flux measurements were directly conducted by determining the covariance of chemical concentration with vertical wind speed, and the response time required for this study was less than 1 s. With GC-PTR-MS, biogenic C_5 and C_6 compounds were also detected after freeze–thaw wounding leaves [32] and lawn mowing [53], respectively.

Plants also commonly emit large amounts and varieties of volatiles after damage inflicted by herbivores. Von Dahl et al. demonstrated that the release of methanol dramatically increases and can be substantially greater than the release of *E*-2-hexenal when *Manduca sexta* larvae attacks *Nicotiana attenuata* plants [54]. Similar results were also obtained during monitoring VOCs induced by *Euphydryas aurinia* caterpillars feeding on *Succisa pratensis* leaves [55]. The emission of ethanol, acetaldehyde, acetic acid, ethyl acetate, 2-butanone, 2,3,-butanedione, and acetone from *Arabidopsis* roots has been identified by both PTR-MS and GC-MS [56]. The rapid release of 1,8-cineole and a monoterpene was demonstrated after compatible interactions of *Pseudomonas syringae* DC3000 and *Diuraphis noxia* with roots. But mechanical injuries to roots did not release any wound-induced VOCs, and the VOCs released were basically the same for the infected and noninfected roots.

VOC emissions from tobacco plants exposed to ozone were investigated with PTR-MS in conjunction with GC-MS, and the formation of volatile C_6 emissions was found to be inversely proportional to the O_3 flux density into the plants [57]. Jasmonic acid, a signaling compound with a key role in both stress and development in plants who elicits the emission of VOCs, was sprayed on the leaves of the Mediterranean tree species *Q. ilex*, and the emissions and uptake of VOCs were detected with PTR-MS and GC-MS after a dark–light transition [58]. Monoterpene and methyl salicylate emissions were enhanced and formaldehyde foliar uptake decreased significantly 24 h after the jasmonic acid treatment. The release of VOCs from eucalypt as a function of temperatures from ambient to combustion were analyzed by PTR-MS, GC-MS, and direct analysis in real time (DART) MS [59]. The biogenic VOCs seem to provide a protection against high temperatures [60] and oxidation stress [61].

Tropical forests are known to emit large quantities of reactive trace gases and aerosols and strongly influence the atmospheric oxidation efficiency and the Earth's climate system. Airborne measurements of isoprene and its oxidation products were performed over the tropical forest of Suriname [62–65]. Isoprene and its degradation products methylvinyl ketone and methacrolein and possibly isoprene hydroperoxides were measured as functions of height and time in day (Figure 28.6), and these results are consistent with the emissions estimated in model calculations [62]. The measurements have also been performed in a productive woodland savanna (Calabozo site, during the wet and dry seasons), a less productive grassland savanna (La Gran Sabana, Parupa site), and a large area of the northern Amazonian rainforest in the long dry season [66,67]. Two times lower levels of isoprene were observed during the dry season and the concentrations of all masses at the

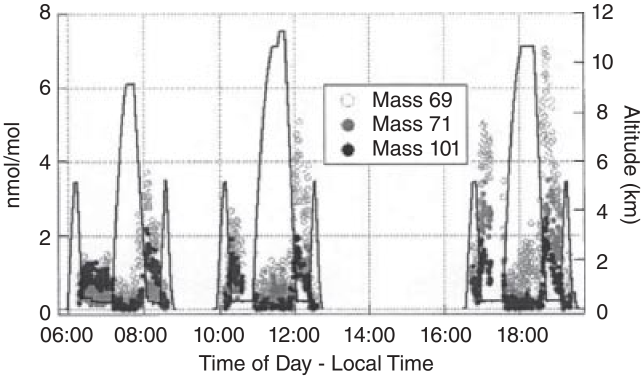


FIGURE 28.6 Concentrations of isoprene (*m/z* 69), methylvinyl ketone and methacrolein (*m/z* 71), and possibly isoprene hydroperoxides (*m/z* 101) as a function of height (full line) and time of day. Reprinted with permission from Reference [62]. Copyright 2000 Elsevier.

Parupa site were about three times lower than those at the Calabozo site during the wet season [66]. Isoprene emission in the tropical rainforest model ecosystem of Biosphere 2 laboratory in a mild water stress, and its relationship with light and temperature were investigated [68]. Gross isoprene production was not greatly affected by mild water stress but dependent on both light and temperature. The daily emission fluxes of 2-methyl-3-buten-2-ol, methanol, acetone, and acetaldehyde from a subalpine forest site in the Rocky Mountains of the United States were 1.5, 1, 0.8, and 0.4 mg m^{-2} h^{-1}, respectively, with the disjunct eddy covariance (DEC) method [69]. DEC can be regarded as a variant of the eddy covariance, and samples were taken almost instantaneously (~0.1 s) and separated by a long time interval ($\Delta t = 10$–30 s).

The vertical concentration profiles of biogenic VOCs in a forest canopy were measured, and there were major differences in VOC emission between daytime and nighttime [70,71]. The canopy fluxes of isoprenoids above the Norway spruce forest were determined by GC and PTR-MS with relaxed eddy accumulation (REA) method [72]. In the use of REA, samples were analyzed at two different reservoirs, which depended on the direction of the vertical wind w ("up-draught" reservoir in case of $w > 0$ and "down-draught" reservoir in case of $w < 0$). Subsequently, the diurnal variation of biogenic VOCs was measured at 12 m (in the treetop) and at 24 m (above the canopy) [73]. By using PTR-MS coupled with the eddy covariance technique and GC-flame ionization detector (FID) with a REA system, the mixing ratios and fluxes of total monoterpenes, from a ponderosa pine plantation [74] and from Scots pine (*Pinus sylvestris*) trees in a boreal coniferous forest [75], were detected. The results measured by PTR-MS were larger than those by GC-FID, indicating that GC-FID only could measure the common, longer-lived monoterpenes well [74]. On-line measurements of VOCs in the European boreal zone were conducted in Hyytiala, southwestern Finland, with PTR-MS [76–78]. The measured VOCs were divided into three classes based on their concentrations: the masses in the first class had a high diurnal variation with maximum values in the afternoon including methanol, acetone, methyl-vinyl-ketone, and hexanal; monoterpenes and phenol belonging to the second class also had a high diurnal variation but with maxima during the night; and the masses in the third class did not have an apparent diurnal variation like benzene [76]. The sesquiterpenes and methyl chavicol were first identified at Blodgett Forest, a coniferous forest in the Sierra Nevada Mountains of California, by PTR-MS and GC-MS [79,80].

The daily methanol emissions were measured above two differently managed grassland fields (intensive and extensive) in central Switzerland [81], and flux measurements of VOCs were performed over agricultural grassland during and after a cut event [82], showing that legume plants and forbs emitted a higher number of different VOC species than graminoids. The exchange of acetaldehyde between forest canopies and the atmosphere was investigated, and it was found that only living leaves could release acetaldehyde, and the emission and uptake of acetaldehyde depended on the ambient acetaldehyde concentrations, stomatal resistance, and the compensation point, which is a function of light/temperature [83].

28.3.1.2 Biomass Burning Biomass burning is also a major source of VOCs in the atmosphere, and more than 80% of the world's biomass burning takes place in the tropics as a result of savanna fires, forest fires, and the burning of agricultural waste and woods [84]. The concentration of acetonitrile was measured via GC-PTR-MS off the U.S. west coast, over California, and during two transfer flights over the United States in April and May of 2002 [85]. And it was found that acetonitrile was greatly increased in the plumes from two forest fires, suggesting the availability of the measurement of acetonitrile as an indicator for biomass burning emissions [86,87]. The emission ratios of CO, a general tracer for incomplete combustion, to acetonitrile in the plumes were respectively 2.0 ± 0.3 ppt/ppb for the Utah fire and 2.7 ± 0.4 ppt/ppb for the Yucatan fire, which were slight higher than previously reported values. There is evidence that the ocean is an effective sink for acetonitrile by dissolving in the upwelling ocean water or by biological processes in the surface water [85,88].

The relative abundance of acetonitrile to that of CO was also obtained in the Indian Ocean, showing a strong biomass burning impact in western India, mixed pollution sources in northeast India, and the dominance of fossil fuel combustion in the Middle East [89]. And it also suggested that the abundances of acetone and acetaldehyde were from unidentified sources both in biomass burning and in remote marine air. High concentrations of acetonitrile over Venezuelan woodland savannah were detected [90]. Most likely it was released from the warm waters of the Caribbean Sea. So acetonitrile concentrations probably will still be much higher in biomass burning plumes, indicating the general suitability of acetonitrile as a biomass burning marker should be treated with caution.

Karl et al. detected VOCs at the Mauna Loa Baseline Station in March/April 2001 and thought that the abundance of acetone seemed to be partly influenced by biomass burning and domestic biofuel emissions [91]. It was revealed that secondary production of acetone and methanol in fire plumes over the Mediterranean could also be thought as characteristic biomass burning signatures, and the emissions of 25–31 and 29–35 Tg/year for acetone and methanol were estimated, respectively [87].

The Tropical Forest and Fire Emissions Experiment (TROFFEE) used laboratory measurements, followed by airborne and ground-based field campaigns during the 2004 Amazon dry season, to quantify the emissions from pristine tropical forest and several plantations as well as the emissions of fuel consumption and fire ecology of tropical deforestation [92]. The inorganic and non-methane organic compounds were measured to derive biomass burning emission factors [92–94] by UV absorbance, Fourier transform infrared spectroscopy (FTIR) and PTR-MS, and higher concentrations of oxygenated VOCs than previously included in chemical-transport models were found [93].

28.3.1.3 Ambient Air The measurements of atmospheric VOCs from a wide variety of aircraft, ship-, and ground-based platforms have been reviewed by de Gouw and Warneke [11]. Here, some of the research applications in the ambient air will be described. The diurnal variation of the mixing ratios of VOCs in ambient air at the western outskirts of Innsbruck was monitored [95,96]. The abilities to detect peroxyacetic nitric anhydride (PAN), peroxypropionic nitric anhydride (PPN), and peroxymethacrylic nitric anhydride (MPAN) on-line in ambient air with SIFT-MS and PTR-MS were also demonstrated [97]. Through the measurements of PAN, PPN, and MPAN, the contributions of biogenic hydrocarbons and anthropogenic hydrocarbons to regional tropospheric ozone production could be estimated. The measurements of VOCs to describe the variability–lifetime relationship and to indirectly estimate an average OH concentration, the most important atmospheric oxidant, were investigated [98,99], and anthropogenic VOCs such as benzene and toluene were detected in ambient air [100–102]. GC-PTR-MS has been used to prove that a number of common atmospheric VOCs could be accurately detected by PTR-MS with a fast response time [103–105]. The atmospheric trace gas measurements over the Indian Ocean were performed by PTR-MS and atmospheric pressure chemical ionization mass spectrometer (AP-CIMS) [106]. The ocean's emissions of VOCs were also detected [107–109]. The oceanic emission and uptake of VOCs in the atmosphere were investigated [107], and the photosynthetically active radiation and biological parameters should be considered in estimating the influence of the global ocean on atmospheric VOC budgets. Due to the potentially limited ozone production, the concentrations of VOCs at Cape Grim from the Southern Ocean were significantly lower than that observed over the remote tropical ocean in the northern hemisphere [109]. The measurements of CO, NO, NO_2, benzene, toluene, and PM_{10} at a motorway location in the Alpine Inn Valley were performed to consider vehicle emission influences on air pollutant levels [110,111]. The formaldehyde was measured in various meteorological and photochemical conditions at Mount Tai, China, in June 2006 [112]. NO^+ was also employed as the reagent ion in PTR-MS to detect 1,3-butadiene in the air [113].

Urban and suburban VOC measurements have been made in many cities including Caracas [114], Tokyo [115], Mexico [116–119], Barcelona [120,121], and Manchester [122]. Measurements of VOCs in Caracas and the other suburban, rural, and remote regions showed that vehicle exhaust was the major source of aromatic compounds, and biomass burning seemed to make an important contribution during the dry season [114]. Seasonal variation of VOCs in Tokyo was measured by GC-FID and PTR-MS, indicating that the concentrations of oxygenated VOCs in summer were higher than those in autumn, whereas there was little difference in the aromatic hydrocarbons emission due to the changes of seasons [115]. Therefore, the enhanced photochemical reactivity in summer could be deduced. Diurnal patterns of VOC emission in Mexico City were obtained, showing that vehicle exhaust was also the main source of VOCs [116–118] and suggesting that some alkanes were underestimated in the emissions inventory, while some olefins and aromatics were overestimated in comparison with the VOC lumped emissions reported in other photochemical air quality modeling studies [117]. The daily, weekly, and seasonal variations of VOC release in the vicinity of a highway of Barcelona were monitored, and the results provided useful information on the dynamics of VOCs atmospheric concentrations in this area, representative of the Mediterranean region, where there was frequently high levels of ozone in summer [121].

Gas samples from room air were also detected with PTR-MS to estimate the indoor air quality [4,123]. Samples were taken from five rooms constructed more than 20 years ago. Two rooms had been equipped with new furniture and carpets only 2 months before the measurements were done. The concentrations of formaldehyde and ethanol were quite similar in the old and newly furnished rooms. Acetaldehyde, methanol, propanol, acetone, and toluene were strongly enhanced in the two newly furnished rooms. It was also found that the concentration of formaldehyde in four of the five rooms was higher than the maximum concentration allowed by Austrian law for permanent exposure dose to human [4].

PTR-MS has also been used to study the mechanism of atmospheric chemistry. Northway et al. found unexpectedly high values for acetaldehyde in the airborne measurements and the acetaldehyde increasing with the ambient ozone levels in the free troposphere [124]. They suggested the heterogeneous oxidation of a number of unsaturated organic compounds might serve as a possible source for a chemical artifact produced in the instrument inlet. The gas-phase products from the reaction between terpenes (α- and β-pinene) and OH radicals in the presence of NO_x were analyzed with PTR-MS [125] on-line. The products formed at different conditions were measured in the simulated aircraft cabin [126–128]. The acetone, nonanal, decanal, 6-methyl-5-hepten2-one, geranyl acetone, and 4-oxopentanal were the characteristic gas-phase products formed when ozone was added to the cabin air [126,128].

There are many laboratory chamber studies to investigate the formation mechanisms of secondary organic aerosols (SOAs) with PTR-MS [129–133]. Baltensperger et al. investigated the SOA formation from the photooxidation of 1,3,5-trimethylbenzene α-pinene at the smog chamber and found that oligomerization was a key SOA formation mechanism [132]. The first- and second-generation oxidation products, in the formation of aerosols from the ozonolysis and photooxidation of 16 biogenic hydrocarbons, were analyzed [129]. All the products could be classified into two groups based on the number of double bonds of the hydrocarbon: (1) compounds with only one double bond. SOAs were formed mainly from low volatility first-generation oxidation products due to rate limiting in the first oxidation step; and (2) compounds with more than one double bond. Because the second oxidation step might also be rate limiting, second-generation products contributed substantially to SOA growth. The gas-phase VOCs produced by the ozonolyses and photooxidation of a series of terpenes have also been monitored [130,131]. A new method for the measurement of SOA formation at low total organic mass concentration (<10 μg/m) was developed using PTR-MS coupled with particle measurements [133]. And it has been found that extrapolations of current partitioning models to the conditions of low total organic mass concentration significantly underestimated SOA production under dark and low-NO_x conditions and overestimated SOA production under light and higher NO_x conditions. The particulate phase of an aerosol was analyzed by PTR-MS with a modified inlet system at a high time resolution [134]. The new inlet mainly consisted of a denuder to strip off the gas phase, and a heater (120/150°C) to vaporize the aerosol particles.

28.3.2 Food Research

PTR-MS has been applied to monitor emission of VOCs in the field of food research. The potential utility of PTR-MS in food science was first recognized by its initiating research team in Innsbruck. Now there are many investigations on the flavor studies and on the assessment of food quality.

28.3.2.1 VOCs Released from Food To better understand the concept of flavor perception requires the identification of the VOCs released from the food, which generate a characteristic aroma perceived by the nose. The initial investigation was to monitor breath sample by means of PTR-MS after fruit digestion [135,136]. Excessive quantities of methanol were detected, which were due to the presence of pectin in the fruits, and the high concentration of methanol would result in the development of nonalcoholic cirrhosis of the liver. Similarly, allyl methyl sulfide, allyl methyl disulfide, diallyl sulfide, diallyl disulfide, diallyl trisulfide, dimethyl sulfide, and acetone were found in the breath gas after the garlic was ingested [137]. The concentrations of those compounds were monitored during the consumption of garlic, and the variation of acetone versus time was obtained. The significant increase of acetone in the breath might be relevant to enhanced metabolism of serum cholesterol, triglycerides, and total lipids in the bloodstream. In a word, through monitoring VOCs in human breath, it could be possible to understand specific metabolic processes during food digestion. The release of VOCs during eating of banana has been compared with its headspace gas concentration profiles [138]. Nosespace air was sampled during eating via two glass tubes fitted into the nostrils. Both ripe and unripe bananas were considered. Isopentyl and isobutyl acetate were found to be characteristic of ripe banana, but 2*E*-hexenal and hexanal were typical of unripe banana. Significant differences between the headspace and nosespace measurements were also found for both ripe and unripe bananas.

Subsequent work by van Ruth and coworkers has investigated how four pectin-containing systems with different structures and strengths affected the release of aroma compounds in an artificial model mouth and in the nose of an assessor [139]. It was suggested that mastication and saliva had a large influence on how much of the aroma compound was released from the mouth to the nose. Afterward, the influence of mastication rate on the dynamic release of seven volatile flavor compounds from sunflower oil was evaluated in a model mouth [140]. The influences of water on flavor retention were also evaluated [141]. The dehydration and subsequent reconstitution of mandarin juices were discriminated by their mass spectra with the help of principal component analysis (PCA). The volatile flavor retention was studied during consumption of custard desserts. Mestres et al. also studied the correlation between retronasal perception and the sensory perception during and after consumption of whey protein gels [142].

Another area of food research is the study of flavor perception. This involves attempts to detect VOCs emitting from foods on-line, with the flavor characteristics perceived by human beings, and to quantify the concentrations of flavor compounds with PTR-MS. To date, only a few specific groups have been studied mainly including foodstuffs, vegetables, and dairy products.

Lindinger et al. were the first to investigate on the emissions from foods, and the coffee headspace was analyzed due to its variety and complexity [6]. A 2-g sample of freshly ground coffee was put into a 100-mL glass, and clean air was allowed to flow through the headspace at a rate of 500 cm^3/min, and the headspace was monitored before and after 90 g of water at 17°C was added to the coffee powder. The VOC emissions during coffee roasting at different temperatures were also measured in real time [143]. The mass spectra detected from a particular coffee brew were detected, suggesting that a large number of VOCs existed in the coffee headspace. And their identification is a particularly challenging work because of isobaric interferences and possible ionic fragmentation. A series of approaches and strategies was used to identify chemical compounds including the PA change by switching H_3O^+ to NH_4^+, the use of energy-dependent breakup patterns by changing *E/N*, and using liquid–gas partition coefficients according to Henry's law [144,145]. As a result, 64 distinct compounds were identified in the coffee headspace, which is an impressive achievement for PTR-MS.

In addition to coffee, the Lindinger group also investigated methanol, ethanol, acetaldehyde, acetic acid, propanol, and acetone (involving some propanal) in the headspace of strawberry, white currant, raspberry, and blackberry, as a function of time [6]. Later on, the release of strawberry flavor compounds from pectin and gelatin gels was also evaluated by instrumental and sensory analysis [146]. Similarly, volatile flavor measurements of rehydrated red bell peppers [147], three grana cheeses [148], red kidney beans [149], kidney beans and soybeans [150], medium-chain triglycerides and sunflower oil [151], starch [152], cheese crackers [153], olive oils [154], raspberry and its juice [155], and palm wine (*Elaeis guineensis*) [156] were also carried out with PTR-MS.

In other flavor perception studies, the PTR mass spectra of the headspace of seven different brands of mozzarella cheese held at 36°C have been first compared with the judge panel flavor profile [157]. A PCA of the mass spectral data was used to discriminate different cheese types. And a trained panel of sensory judge was employed to give qualitative and quantitative analysis of mozzarella cheese. It was found that there was an interesting and clear similarity between the classical sensory and the instrumental analysis. More recently, a robust and reproducible model was developed to predict the sensory profile of espresso coffee, and the model was derived from 11 different espresso coffees, which had been analyzed by a trained panel and PTR-MS, and further validated using eight additional espressos [158]. Flavor studies of whey [159], custard desserts [160], other types of cheeses [148,161], milk [162], wine [163,164], apples [165], olive oils [166], bread [167], and butter and butter oil [168,169] were also conducted by the PTR-MS system.

Incidentally, it is difficult to identify all compounds with PTR-MS in flavor analysis, because there may be isomeric/isobaric interferences and, to some extent, ion fragmentation. In general, a variety of compounds including aldehydes, ketones, alcohols, and esters might contribute to the flavor profile. And a detailed study of the fragmentation behavior of 53 flavor compounds under typical operating conditions of PTR-MS was investigated [170]. Fragmentation pattern dependence on *E/N* in PTR-MS was reported for 21 ester compounds [171].

28.3.2.2 Food Quality Assessment PTR-MS can be applied in the field of control of food quality. If some foods are not stored properly at low temperature, then unpleasant odor from foods would emanate as they undergo decay. The VOC emissions, associated with microbial growth, are indicative of deterioration. So the change in odor should be reflected by the VOC emissions. PTR-MS provides a simple, fast tool to assess the extent of decay through detecting the relevant VOCs.

The first application of PTR-MS to assess degradation of beef meat was carried out by the founders of this technique [6,172]. Five VOCs were monitored for about 63 h as the beef kept at room temperature decays. It was found that sudden production after a little more than 1 day and then significant increase of methanethiol was especially noticeable. The researchers preliminarily suggested that the meat was still safe to consume as long as the methanethiol concentration remained below that of dimethyl sulfide. Thus, monitoring the concentrations of some compounds in the headspace is helpful to assess the freshness of the meat.

Subsequent study on the decay process of meat using PTR-MS has been done by Mayr et al. [173,174]. The authors investigated the spoiling of the air- and vacuum-packed beef and pork stored at 4°C through simultaneously monitoring the viable counts by the microbiological standard technique and the VOC emissions with PTR-MS. The VOC emissions were found to be different depending on the packaging conditions. For air-packaged beef and pork, peaks at *m/z* 63, which might be the protonated dimethyl sulfide, and at *m/z* 91, likely the protonated diethyl sulfide, thioacetic acid methyl ester, or 2,3-butanediol, were found to be the typical spoiling compounds emitted under aerobic conditions for the air-packed meats, and the spoilage was dominated by aerobic bacteria *Pseudomonas* spp. and Enterobacteriaceae. Whereas under anaerobic conditions, ethanol was the characteristic VOC for vacuum-packed meats, and anaerobic *lactic acid bacteria* is active. In addition, the concentration of VOC at *m/z* 63 versus the number of total aerobic viable bacteria in air-packaged beef at different storage time was also obtained, suggesting that PTR-MS is promising to provide a rapid and quantitative assessment of spoilage effect of foods [173].

Moreover, PTR-MS has also been successfully applied to investigate ripening for strawberries, blackberries, raspberries, blueberries, and white and red currants [175]; to assess aging of cheese [176]; to determine the quality of herb extracts [177]; to monitor fermentation processes in apples [178]; to distinguish between healthy and defective olive oil [179], different types of orange juice such as untreated, flash-pasteurized, juice-pasteurized, and high-pressure-treated juices [180], and between different types of strawberries [181–183]; and to monitor VOC changes during storage of cheese crackers [184]. It demonstrated again that PTR-MS has the powerful ability to control the quality of food.

In addition to determining markers of food decay and ripening, PTR-MS headspace measurements can also be used to assess the effect of treatment on food. It has been reported by Jaksch et al. that the ozone treatment reduced the bacterial growth and hence extended the shelf life of pork meat [185]. The signal detected at *m/z* 63 for the protonated dimethylsulfide was found to strongly increase with time for untreated meat, whereas ozone-treated meat showed significant signal reduction, suggesting that microbial activity was greatly suppressed by ozone treatment. However, the bacterial numbers were very high, independent of the treatment. These results indicated that the microbial activity was greatly suppressed by ozone treatment, but the effect was limited and unable to produce a lethal damage to microorganisms in meat. Therefore, the ozone treatment at the dose levels employed would be insufficient to sterilize meat, and monitoring VOC emissions to assess bacterial levels in meat products might not be appropriate enough. Similarly, the effect of supercritical CO_2 and N_2O pasteurization (100 bar, 36°C, and 10-min treatment time) on the microbial and sensorial quality of fresh apple juice was also investigated [186]. Headspace analysis, performed by both GC-MS and PTR-MS, indicated that CO_2 and N_2O treatments induced some ester (acetates) and aldehyde reduction, which might be responsible for the changes in the flavor of treated juices.

The release of acrylamide has been detected in real time during thermal treatment (120–170°C) of potato via the Maillard reaction between an amino acid and a reducing sugar, and acrylamide has been classified as "probably carcinogenic to humans" [187]. The formation of acrylamide was found to be affected by the choice of ingredients, their physical state, the reaction temperature, and the reaction time during the cooking process in their follow-up study [188]. The influence of starch hydrolysis by α-amylase addition on structural properties and aroma release have been studied [189]. Only a slight increase in headspace intensity of menthone after a 60-min starch hydrolysis was found, which might be influenced by the viscosity effects, interaction among aroma compounds, and starch degradation.

28.3.3 VOC Detection in Water

Up to now, there are few applications on detecting VOCs dissolved in liquid samples with PTR-MS. The PTR-MS is designed only for trace gas detection and is not suitable for direct liquid sample introduction. Two methods have been obtained for the PTR-MS measurements of VOCs in liquid (1) by a membrane inlet proton transfer reaction mass spectrometer (MI-PTR-MS) [190–192] or (2) by measuring the solution headspace and then calculating the concentration in the liquid using Henry's law constant (HLC) [145,193–195].

28.3.3.1 MI-PTR-MS The MI-PTR-MS platform was first explored by Alexander and coworkers [190]. A membrane of polydimethylsiloxane (PDMS) was employed in the MI-PTR-MS as an interface that can penetrate some organic chemicals easily while others may show little or no permeation. With the MI-PTR-MS, the fundamental properties like diffusion and partition coefficients have been determined for different chemical compounds both in nonpolar and polar species [190,191]. If the analyte–membrane interaction is stronger, then the smaller diffusion coefficient and larger partition coefficient will be obtained. The effect of the temperature in the range of 25–65°C on the diffusion and partition coefficient has also been investigated. The detection limit of the MI-PTR-MS system was in the order of tens of ppt, and its response was linear for more than four orders of magnitude. This study demonstrated that MI-PTR-MS has the ability to measure VOCs dissolved in aqueous solutions [191].

The PDMS hollow fiber membrane, with an internal diameter (i.d.) of 0.30 mm, an outer diameter (o.d.) of 0.64 mm, and a length of 8.2 cm, was used as an interface between the aqueous sample and the drift tube of the PTR-MS to detect VOCs in water [192]. Its schematic diagram is shown in Figure 28.7. Seven compounds, methanol, acetonitrile, acetone, dimethyl sulfide, isoprene, benzene, and toluene, were prepared in both fresh and salty water at various concentrations from 0.1 to 1000 parts per billion by weight (ppbw). The liquid sample was continuously supplied to the membrane inlet via a peristaltic pump at a flow rate of 10 mL/min at atmospheric pressure. The analytes that permeate through the membrane were transported to the drift tube by zero air carrier gas at 10 mL/min. The transfer line connecting the inner side of the membrane to the drift tube region was heated up to 60°C. And the other parts were kept at room temperature. PTR-MS instrument operated at the standard conditions: drift tube voltage 600 V and pressure in drift tube 2.0 mbar. All the experiments were performed using the selected-ion-mode operation of the PTR-MS.

It was noted that if the air bubbles were present in the sample, then the concentrations might show momentary increases. This phenomenon was more apparent for those compounds having lower solubility in water (see Figure 28.8). So the air bubbles in the sample must be avoided.

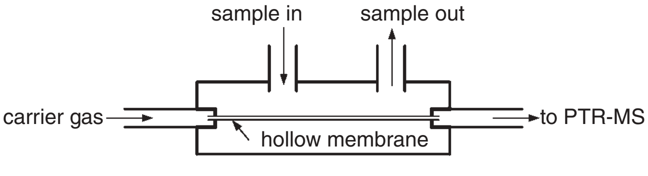


FIGURE 28.7 Schematic representation of MI-PTR-MS.

The experiment was done with various compounds at concentrations from 0.1 to 1000 ppbw, and in all the cases, no matrix effect due to the salt in seawater was observed. Therefore, seven VOCs could be detected simultaneously both in fresh and in salty water. The permeability through the membrane was the main factor limiting the detection sensitivity toward specific compounds. In this MI-PTRMS system, the limit of detection was at about 100 pptw for DMS at a signal-to-noise ratio 3.

Besides good sensitivity, the MI-PTR-MS also has a wide linear dynamic range for all the VOCs analyzed in water and seawater. The data in Table 28.2 illustrate a linear response of up to four orders of magnitude, suggesting that the MI-PTR-MS can quantify VOCs with various concentrations dissolved in water. However, as to MI-PTR-MS technique, compared with direct inlet PTR-MS as used in atmospheric monitoring and food science, its deficiency is a much slower response time even up to several minutes.

28.3.3.2 Quantify VOCs in Water Using HLC Henry's law describes a dynamic equilibrium between the concentration of the solution and the partial pressure in the headspace above the solution. HLC (or H) is most commonly defined as

$$\mathrm{HLC} = c_a/p_g, \tag{28.24}$$

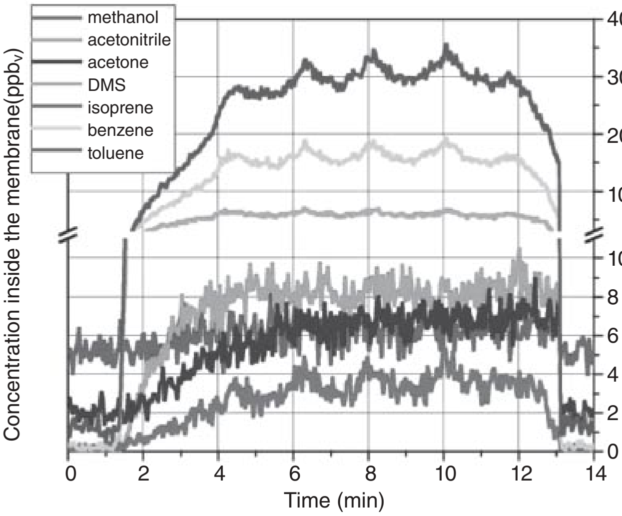


FIGURE 28.8 Appearances of discontinuous increases in concentration due to air bubble presence in the water sample, especially for hydrophobic compounds like toluene, benzene, and isoprene. DMS, dimethylsulfide. Reprinted with permission from Reference [192]. Copyright 2004 Elsevier.

TABLE 28.2 The Concentrations (ppbv) of Seven VOCs Measured by the MI-PTR-MS Versus Concentrations (ppbw) in Fresh and Salty Water at Room Temperature

Liquid Sample (ppbw)	1000		100		10		1		0.125	0.1
Detected by MI-PTRMS (ppbv)	Fresh Water	Salty Water	Fresh Water	Salty Water	Fresh Water	Salty Water	Fresh Water	Salty Water	Fresh Water	Salty Water
Methanol	3.30	3.66	0.39	0.40	–	0.16	–	–	–	–
Acetonitrile	88.0	94.1	9.43	9.56	0.73	0.94	0.09	0.11	–	–
Acetone	47.0	53.4	5.00	5.21	0.45	0.56	–	–	–	–
DMS	488	499	51.3	48.0	4.77	4.83	0.47	0.50	0.07	0.06
Isoprene	61.2	60.7	5.80	4.65	0.53	0.52	–	0.07	–	–
Benzene	204	203	22.2	18.9	2.15	1.83	0.19	0.23	–	–
Toluene	303	314	30.1	28.7	2.61	2.99	0.28	0.30	–	–

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where c_a is the concentration of a species in the aqueous phase (mol/L), and p_g is the partial pressure of the same species in the gas phase in the headspace (atm). The HLC is given in units of mol/L/atm. Once the HLCs and the partial pressure p_g are known, the concentrations in the solution can be obtained.

The HLC measurements of 18 VOCs were first described by Karl et al. using dynamic sampling PTR-MS [193]. Currently, there are two common experimental approaches to measure HLCs. The first is based on the static determination of headspace concentrations, thus called headspace technique. However, the equilibrium between the liquid and the gas phase may get perturbation especially in the case of low vapor pressures when headspace samples are extracted. This may result in an overestimation of the measured HLCs. An advanced dynamic technique has been adopted to determine partition coefficients. A gas flow passed through a solution with dissolved VOCs, and VOCs can be extracted into the bubbles, leading to a decrease of their liquid concentration. By measuring the gaseous concentration of VOCs versus time, partition coefficients can be calculated. There are two methods to determine the HLCs. (1) For highly volatile compounds (HLC < 1 mol/L/atm), the partition coefficient can be determined with good accuracy within about an hour using single stripping cell configuration. HLCs can be obtained in the following form:

$$\ln\left(\frac{cps_t}{cps_0}\right) = -\frac{Q}{HVRT}t, \tag{28.25}$$

where cps_t is the count rate of (VOC)H$^+$ at time t, cps_0 is the initial count rate of (VOC)H$^+$ at time $t = 0$, V is the liquid volume, Q is the airflow rate through the vessel, T is the temperature, and R is the molar gas constant. (2) For low volatile compounds (HLC > 10 mol/L/atm), the slope of an $\ln(cps_t/cps_0)$ versus t plot can be very small. So the time must exceed 10 h to make a reliable measurement of HLCs. A double stripping cell has been developed, which allows fast determination without compromising the accuracy. In this case, HLCs can be calculated from the slope of an $\ln(1 - cps_t/cps_0)$ versus t plot:

$$\ln\left(1 - \frac{cps_t}{cps_0}\right) = -\frac{HQ}{VRT}t. \tag{28.26}$$

In 2003, the HLCs for six volatile coffee flavor compounds in pure water and in liquid coffee were measured with dynamic measurements [145]. The partition coefficients in pure water and coffee were significantly different for ethyl-2-methylbutyrate and barely different for 2-methylpropanal. For 2-methylbutanal, 3-methylbutanal, dimethyl sulfide, and dimethyl disulfide, however, the values were indistinguishable in pure water and coffee within the experimental precision. Moreover, this method was first used to measure acetone concentrations in the surface seawater by Holzinger et al. [194]. At present, the detailed description about the quantification of dissolved dimethyl sulfide in seawater using HLC was reported in 2009, and the HLC of dimethyl sulfide and its temperature dependence were considered [196]:

$$\mathrm{HLC} = \mathrm{HLC}_0 \times \exp\left[\frac{-\Delta_{\mathrm{soln}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{28.27}$$

where HLC_0 (0.42 M/atm) is the HLC under standard conditions ($T_0 = 298.15$ K), $\Delta_{\mathrm{soln}}H$ is enthalpy of solution, R is the gas constant, and $-\Delta_{\mathrm{soln}}H/R$ was estimated to be 3593 K.

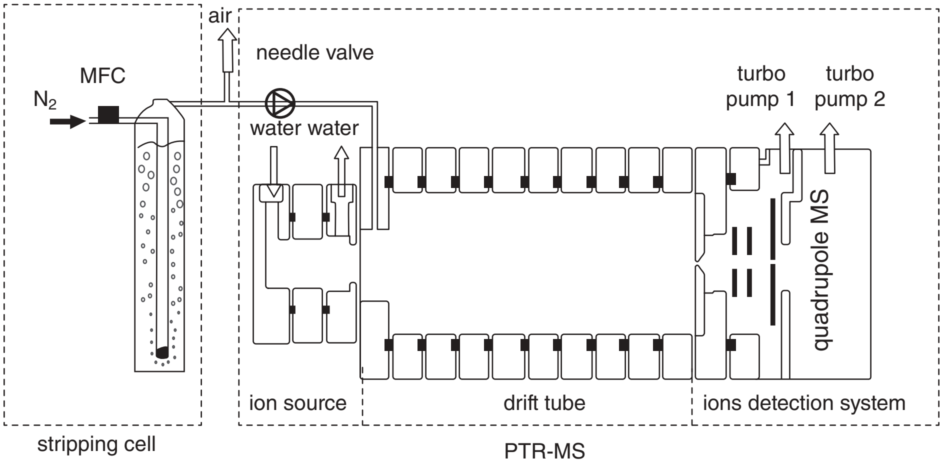

FIGURE 28.9 Schematic diagram of the PTR-MS apparatus coupled with dynamic gas introduction from a liquid simple. MFC, mass flow controller. Reprinted with permission from Reference [195]. Copyright 2008 Acta Physico-Chimica Sinica.

In our research group, HLCs of 11 aromatic compounds using PTR-MS were detected with the dynamic technique [195]. The setup is shown in Figure 28.9. The concentrations of benzene dissolved in water were measured by the PTR-MS in combination with Henry's law, and the results are in agreement with the calibration concentrations. Although the HLCs for compounds over a wide range of volatility can be rapidly obtained, the same VOCs dissolved in different liquids may have different HLC values due to matrix effects. Therefore, further investigations will be needed for VOC detection in liquid environmental samples by means of Henry's law.

28.4 CONCLUSIONS AND PROSPECT

PTR-MS is a powerful technique for the trace VOC measurement with the advantages of soft ionization, rapid response, absolute quantification, and high sensitivity. The great versatility of its on-line detection capacity in the environmental fields has been demonstrated including atmospheric monitoring, food research, and water detection. In addition, some methods to distinguish isomeric/isobaric compounds in practical applications have also been reviewed, including changing *E/N*, using new reagent ions like NH_4^+, two-stage PTR-MS, PTR-IT (LIT, TOF)-MS, and GC-PTR-MS.

At present, PTR-MS instruments are available in laboratories all over the world and are used to detect VOCs under various circumstances more or less relative to basic researches. In the future, further development of the PTR-MS technique will likely involve higher performance. Meanwhile, PTR-MS will be extended to include more application fields in addition to environmental VOCs monitoring. It is not surprising that someday PTR-MS could undertake the measurement of some compounds in a liquid or solid sample.

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