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Optimization and sensitive detection of sulfur compounds emitted from plants using proton transfer reaction mass spectrometry

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ABSTRACT

Proton transfer reaction mass spectrometry (PTR-MS) is employed as a highly sensitive detection method for trace gas analysis of sulfur compounds. The effects of drift tube humidity and the reduced electric field (*E*/*N* value) were evaluated to measure traces of methanethiol, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) under optimal conditions. The three sulfur compounds showed a maximum intensity of the product ion signal at a low fraction of the protonated water clusters as compared to the total reagent ion signal. For methanethiol, DMS and DMDS the highest intensity was observed when the percentage branching ratio of $H_3O^+{\cdot}H_2O$ with total reagent ion signal was 3%, 5% and 3%, respectively. The methanethiol signal dropped sharply with an increase in $H_3O^+{\cdot}H_2O$ while DMS and DMDS showed a less strong dependence. This could be explained by their difference in proton affinity as compared to that of the water cluster (methanethiol 773 kJ mol^{-1}, DMS 830 kJ mol^{-1}, DMDS 815 kJ mol^{-1}, $H_2O{\cdot}H_2O$ >800 kJ mol^{-1}). Taking into account the mean kinetic energy in the drift tube (19 kJ mol^{-1}), the direct proton transfer reaction between DMS or DMDS and $H_3O^+{\cdot}H_2O$ is possible, in contrast to methanethiol. The PTR-MS was used to monitor trace gas emissions of methanethiol, DMS and DMDS emitted from *Brassica rapa* plants in real time. The concentrations of these sulfur compound emissions are in the part per billion range (ppbv) and optimization of the instrument for these compounds helps to measure the low concentrations emitted from control and infested plants. The plant roots were infested with *Delia radicum* larvae and all three sulfur compounds showed an immediate rise in the ion signal intensity after infestation, indicating that the plants were reacting after the roots were damaged by the insects. The sulfur compound emissions lasted for 30 h.

1. Introduction

Proton transfer reaction mass spectrometry (PTR-MS) is a mass spectrometric technique wherein molecules are ionized via a soft chemical reaction. Within this reaction a proton is transferred from the primary ion (H_3O^+) to a neutral molecule. PTR-MS has several advantages as compared to other mass spectrometric methods: no need for sample preparation (such as for GC–MS); low fragmentation due to the soft ionization process; a high sensitivity, down to parts per billion levels (ppbv); fast response time (seconds). The latter makes possible real time analysis and simultaneous monitoring of several volatile compounds. Owing to these advantages it has become a powerful tool for the analysis of volatile organic compounds (VOCs) in a wide range of research fields, such as plant research [1–4], food and flavor research [5], environmental research [6] and breath analysis [7].

Here we use the PTR-MS to monitor emissions from damaged roots and shoots from a variety of plant species [8]. Namely, species of the *Brassicaceae* family; this family contains 330 genera and about 3700 species. The plants are a very important food crop, with many common foods originating from this family: e.g. flower part (broccoli or cauliflower), leaves (cabbage or collard greens), buds (Brussels sprouts or cabbage), roots (rutabaga or turnips), stems (kohlrabi) and seeds (mustard seeds or rapeseed) [9].

Upon herbivore attack, *Brassica* plants emit different VOCs, including aldehydes, ketones, alcohols, carboxylic acids, esters, nitriles and sulfur containing compounds [10]. The latter two compounds (nitriles and sulfur compounds) are considered to be break down products of glucosinolates, a class of plant-produced organic

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compounds that are typical of *Brassicaceae* family species [8]. Glucosinolates are non-volatile compounds. Myrosinase, a root tissue enzyme, breaks glucosinolates into volatile compounds after plant damage by herbivores [11]. Among the VOCs emitted from infested *Brassica* plants, sulfur compounds such as methanethiol (m/z 49), dimethyl sulfide (DMS, m/z 63) and dimethyl disulfide (DMDS, m/z 95) were considered as biomarkers for this infestation. Crespo et al. show the release of these compounds when *Brassica* plants are infested by larvae *Delia radicum* [3].

The main goal of this study is to find the optimal settings for measuring trace amounts of these sulfur compounds. The heavy sulfur atom (32 Da) provides a different functional group compared to, more common, organic compounds. In recent studies, researchers analyzed how the operating conditions of a PTR-MS affect the observed product ions of a variety of chemical compounds [12–15]. In the drift tube three types of reaction are possible between the neutral molecules and the reagent ions that can result in protonated analyte molecule. The relative probability of these three reactions depends on the proton affinity and dipole moment of the neutral analyte, as well as the relative availability of reagent ion cluster species. The primary reaction is simple proton transfer from a hydronium ion to an analyte molecule. This reaction determines whether the compound of interest can be ionized and detected with PTR-MS. This reaction pathway is available when the proton affinity of the neutral exceeds the proton affinity of water (proton affinity of H_2O is 691 kJ mol^{-1} [16]).

$$H_3O^+ + R \xrightarrow{k} RH^+ + H_2O$$

The second reaction is a direct proton transfer reaction from the protonated water cluster, $H_3O^+{\cdot}H_2O$. The reaction produces a protonated monomer ion, along with two molecules of water. For the reaction to be exothermic the proton affinity of the analyte molecule must be larger than the proton affinity of the neutral water cluster. Several values exist in the literature for the proton affinity of the water cluster, we take here the accepted experimental value of 808 ± 6 kJ mol^{-1}, measured with a kinetic method by mass spectrometric means by Goebbert and Wentold in 2004 [17]. We also make use in the discussion of a theoretical value calculated by density functional theory (DFT) by Kawai et al. in 2003 of 833 kJ mol^{-1} [18]. Given discrepancy in these values and the relatively short time between their publication dates and relative advantages of their different methods we include them both in this paper.

$$H_2O{\cdot}H_3O^+ + R \rightarrow RH^+ + 2H_2O$$

The third possible reaction proceeds via so-called ligand switching or clustering, which depends on the dipole moment of the neutral analyte. The dipole moment indicates the feasibility of forming a cluster complex between the neutral analyte and the protonated water cluster. This is the first step in a clustering proton transfer reaction as shown in the equation below. For analyte compounds with proton affinities between water and the water dimer, this reaction pathway is open, provided the cluster complex can be formed. For example, selected ion flow tube (SIFT) studies of acetaldehyde (proton affinity 769 kJ mol^{-1} [16]) show production of protonated parent from the reaction with the monohydrate hydronium cluster ion [19].

$$H_2O{\cdot}H_3O^+ + R \rightarrow R{\cdot}H_3O^+ + H_2O \rightarrow RH^+ + 2H_2O$$

These three possible reaction types cause compounds such as aldehydes, ketones (e.g. acetone), alcohols, aromatics (e.g. benzene), aliphatics (e.g. isoprene) and monoterpenes to have their own reaction dependence when the humidity in the drift tube or the kinetic energy of the ions (E/N-value) is changed. E/N value and humidity influence the reagent ion profile in the drift tube. The E/N value is the ratio of electric field (E) to number density (N) and is presented in units of Townsend (1 Td = 10^{-21} V m^2).

Acetone is easily detected with PTR-MS because it can be protonated by reacting with H_3O^+ or $H_3O^+{\cdot}H_2O$. Warneke et al. observed no dependence on detection sensitivity as a function of humidity [12]. The proton affinity of acetone is 812 kJ mol^{-1} [16], 4 kJ mol^{-1} greater than the value for the water dimer obtained by Goebbert and Wentold [17]. Even allowing for discrepancies in Goebbert's value or taking the higher value of Kawai [18] (833 kJ mol^{-1}) reactions with the protonated water cluster would still be possible due to the relatively high dipole moment of acetone (2.88 Debye [20]) allowing the easy formation of clusters and making available the ligand switch reaction. Contrarily, benzene, is a molecule with zero dipole moment and a proton affinity significantly lower than that of the water dimer reported by either Goebbert or Kawai (750 kJ mol^{-1} [16]), but greater than the proton affinity of water. It can be ionized by H_3O^+, but not very easily by $H_3O^+{\cdot}H_2O$ [12]. The zero dipole moment limits the initial cluster forming step of the ligand switch reaction. Isoprene fragments at high E/N (>110 Td) in the drift tube and forms clusters with the protonated water cluster at low E/N (<110 Td). The proton affinity of this compound is 827 kJ mol^{-1}, high enough to undergo direct proton transfer reactions with $H_3O^+{\cdot}H_2O$ [21], but it does not react with larger cluster ions ($H_3O^+{\cdot}(H_2O)_n$; n = 2,3,4) due to its small dipole moment (0.25 D) [12] and the increased proton affinity of higher order water clusters [18].

Alcohols fragment easily in the drift tube. The initial fragmentation step is often loss of a water molecule (18 Da) with further fragmentation depending on the E/N value. A recent study reported the fragmentation behavior of a series of alcohols, from methanol to 1-hexanol in the drift tube, with a range of E/N from 90 to 140 Td [13]. In a study by Steeghs et al. fragmentation of monoterpenes was observed; the fragmentation patterns varied as a function of the E/N-value. Several monoterpenes with the same protonated monomer mass, m/z 137 were measured and identified by their fragmentation pattern. The monoterpenes alpha (α) and beta (β) pinene, 3-carene and limonene produced fragment ions at masses m/z 67, m/z 81 and m/z 95 [14,15].

The detection efficiency and fragmentation behavior of sulfur containing compounds are unreported so far. Here we investigate the optimal operating conditions to measure and calibrate methanethiol, DMS and DMDS to be specifically used for monitoring emissions from *Brassica* plants.

2. Material and methods

Acetone, benzene, methanethiol, DMS and DMDS were used for this optimization study. Each compound has its own proton affinity and dipole moment, which may cause different reaction pathways with the available reagent ions to be favorable. The details of these compounds are given in Table 1.

100 ppmv concentrations in nitrogen were prepared for methanethiol (m/z 49), dimethyl sulfide (DMS, m/z 63) and

Table 1
Proton affinities and dipole moments of acetone, benzene, methanethiol, DMS and DMDS together with the proton affinities and dipole moments for water and $H_2O{\cdot}H_2O$.

Compound	Proton affinity (kJ mol^{-1}) [16]	Dipole moment (Debye) [20]
Acetone	812	2.88
Benzene	750	0
Methanethiol	773	1.52
DMS	830	1.53
DMDS	815	1.85
Water (H_2O)	691	1.855
$H_2O{\cdot}H_2O$	808 [17]/833 [18]	4.024 [22]

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