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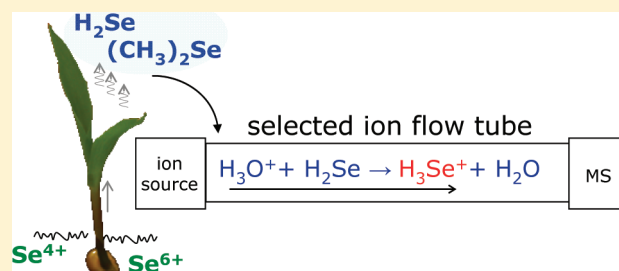
Real-Time Quantification of Traces of Biogenic Volatile Selenium Compounds in Humid Air by Selected Ion Flow Tube Mass Spectrometry

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ABSTRACT: Biological volatilization of selenium, Se, in a contaminated area is an economical and environmentally friendly approach to phytoremediation techniques, but analytical methods for monitoring and studying volatile compounds released in the process of phytovolatilization are currently limited in their performance. Thus, a new method for real time quantification of trace amounts of the vapors of hydrogen selenide (H_2Se), methylselenol (CH_3SeH), dimethylselenide ($(\text{CH}_3)_2\text{Se}$), and dimethyldiselenide ($(\text{CH}_3)_2\text{Se}_2$) present in ambient air adjacent to living plants has been developed. This involves the characterization of the mechanism and kinetics of the reaction of H_3O^+ , NO^+ , and O_2^{+} reagent ions with molecules of these compounds and then use of the rate constants so obtained to determine their absolute concentrations in air by selected ion flow tube mass spectrometry, SIFT-MS. The results of experiments demonstrating this method on emissions from maize (*Zea mays*) seedlings cultivated in Se rich medium are also presented.



Selenium (Se) is an essential nutrient in physiology, but this element can become toxic at elevated concentrations due to its chemical similarity to sulfur. This can lead to a nonspecific replacement of sulfur by selenium in proteins and some other compounds important to all living organisms. Se has become an element of global environmental and health concern because of its toxicity to living organisms and the extensive use in industrial activities. Removal of Se containing toxins from contaminated water and soil using physical, chemical, and engineering techniques is quite complicated and expensive,¹ but it can be effectively achieved by phytoremediation techniques that include phytovolatilization,² which is based on the ability of green plants and associated rhizobacteria to take in selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}) ions dissolved in water, to assimilate them using sulfur transporters and enzymes, and to transform them into volatile forms, including dimethylselenide, $(\text{CH}_3)_2\text{Se}$, and dimethyldiselenide, $(\text{CH}_3)_2\text{Se}_2$. Consequently, this process reduces the toxicity of selenium; for example, $(\text{CH}_3)_2\text{Se}$ is more than 500 times less toxic than the inorganic forms of selenium as has been demonstrated in studies on rats.^{3,4} It is now well documented that various plants can volatilize^{5–7} or accumulate^{8,9} selenium, and this opens the way for their practical use in environmental remediation.

Analytical methods currently used to study volatile Se compounds released by plants usually involve quantitative trapping of volatile gases in alkaline peroxide liquid traps¹⁰ followed by Se assays using various techniques including atomic absorption spectroscopy^{10–12} (detection limit, 1.0 mg Se/L)

and the mass spectrometric methods ICPMS, HPLC/MS, GC/MS, GC-ICPMS, or ESI-MS.¹³ Solid-phase microextraction, SPME, has also been used to extract volatile Se compounds directly from air avoiding the use of a liquid trap, when the absolute concentrations of $(\text{CH}_3)_2\text{Se}$ and $(\text{CH}_3)_2\text{Se}_2$ were determined using external standards.¹⁴ Hollow fiber protected liquid-phase microextraction¹⁵ was recently reported as another effective method for direct GC/MS analyses of $(\text{CH}_3)_2\text{Se}$ and $(\text{CH}_3)_2\text{Se}_2$ in air. In our experience,¹⁶ the SPME method can be used for accurate absolute quantification only with some difficulties and we suspect that it does not effectively extract highly volatile H_2Se , which we speculate may also be emitted by plants even though this has not yet been observed.

Methylselenol (CH_3SeH) is another possible volatile form of selenium homologous to H_2Se and $(\text{CH}_3)_2\text{Se}$ that are known to be involved in detoxification of Se in human metabolism.¹⁷ In plants, CH_3SeH is an intermediate metabolite involved in the Se-methionine pathway in the biosynthesis of $(\text{CH}_3)_2\text{Se}$. Other volatile Se compounds, including selenoformaldehyde,¹⁸ H_2CSe , and diallylselenide,¹⁹ $(\text{C}_3\text{H}_5)_2\text{Se}$, are not known to be involved in phytovolatilization, and thus, they are not included formally in this study; however, the mass spectra were inspected in order to check for their possible presence.

Received: March 5, 2012

Accepted: May 2, 2012

Published: May 2, 2012



Table 1. Rate Constants of the Reactions of H_3O^+ , NO^+ , and $\text{O}_2^{+\bullet}$ with the Four Volatile Se-Compounds Indicated, Given in the Units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ^a

	molecule	MW	α (10^{-24} cm^3) ^b	μ_r (D) ^b	H_3O^+ [k_c]	NO^+ k [k_c]	$\text{O}_2^{+\bullet}$ k [k_c]
hydrogen selenide	H_2Se	81	3.2	0.63	[1.3]		
methylselenol	CH_4Se	95	5.1	1.29	[2.1]		
dimethylselenide	$\text{C}_2\text{H}_6\text{Se}$	109	9.7 ^c	1.32	[2.5]	2.0 [2.1]	2.3 [2.0]
dimethyldiselenide	$\text{C}_2\text{H}_6\text{Se}_2$	188	12.3	1.70	[2.8]	[2.3]	[2.3]

^aThe k_c values in brackets correspond to the collisional rate constant;^{25,26} k is an experimentally derived rate constant as explained in the Experimental Section. Also included are their molecular weights, MW, polarisabilities, α , and dipole moments, μ_r . ^bValues of α and μ_r are taken from refs 33–36 and rounded. ^c α was calculated according Miller and Savchik.³⁷ We had used the value of the atomic hybrid components, τ , for selenium as $4.59 \text{ Å}^{3/2}$.

Thus, the aim of the present study was to develop a method for real time quantification of several volatile forms of selenium obviating sample collection. The compounds chosen as the volatile forms of Se potentially emitted by plants and included in this study are hydrogen selenide, H_2Se , dimethylselenide, $(\text{CH}_3)_2\text{Se}$, methylselenol, CH_3SeH , and dimethyldiselenide, $(\text{CH}_3)_2\text{Se}_2$.

Selected ion flow tube mass spectrometry, SIFT-MS, has been previously successfully used to quantify other biogenic volatile organic compounds (BVOCs)²⁰ in a range of medical, food science, and security related analyses,²¹ because it allows precise real time quantification of trace volatile compounds in ambient air²⁰ and in exhaled breath.²² SIFT-MS is based on chemical ionization of a continuously flowing air sample diluted in He carrier gas using one of the three precursor ions, H_3O^+ , NO^+ , and $\text{O}_2^{+\bullet}$, reacting selectively with trace gases and vapors during an accurately defined time in a flow tube of a given length. Absolute concentration of reactive compounds present in a sample can be calculated online, in real-time from the ratios of product ion count rates to the precursor ion count rates using known rate constants and the other physical parameters.²³

■ EXPERIMENTAL SECTION

To obtain the absolute concentration of vapors of volatile compounds in real time using SIFT-MS, it is essential to know the rate constants and the primary ion products of their reactions with the precursor ions used for analysis.²³ These parameters can be obtained experimentally by studying the reactions of the precursor ions with standard mixes of the reference compounds when these are available.²⁴ This was done in the present study for $(\text{CH}_3)_2\text{Se}$. The vapor of this compound (purchased from Sigma Aldrich, purity $\geq 99.0\%$ (GC)) was introduced into the SIFT-MS instrument (*Profile 3*, Instrument Science Limited, Crewe, U.K.) via a heated calibrated capillary, and full scan mass spectra in the range of mass-to-charge ratio m/z 10 to 160 covering the molecular weights were acquired. For each precursor ion, three mass spectra were obtained with a total integration time of 60 s. The major ion products were identified, and their count rates were precisely determined in separate experiments using the multi-ion monitoring, MIM, mode at a variable flow rate controlled by a needle valve and monitored by a flow-meter (manufactured by Voegtlin, Aesch, Switzerland).²⁴ The rate constant for the proton transfer reactions of H_3O^+ is equal to the collisional rate constant k_c because these reactions are exothermic by more than 40 kJ/mol.²⁵ Thus, the rate constants for the reactions of H_3O^+ were calculated as collisional (k_c)²⁶ using the dipole moment and polarizability data (see Table 1). The rate constants for the reactions with NO^+ and $\text{O}_2^{+\bullet}$ (k) were then derived from their

experimental decay rates relatively to that for H_3O^+ by injecting all three precursors simultaneously and allowing them to react with the sample introduced at variable concentrations.²⁴ The count rates of H_3O^+ , NO^+ , and $\text{O}_2^{+\bullet}$ were plotted on a semilogarithmic scale as functions of the sample flow rate and the rate constants (k) for the NO^+ and $\text{O}_2^{+\bullet}$ reactions were determined from the relative slopes of these plots.²⁴

The rate constants and product ions for the other compounds were obtained from thermochemical calculations of exothermicities of possible reaction channels²⁷ and from calculations of the collisional rate constants for the exothermic proton transfer reactions of H_3O^+ (k_c) according to Su and Chesnavich²⁶ using the dipole moments and polarizabilities of the reactant molecules. These rate constants, m/z of the precursor, and product ions are then used in the kinetics library in the format required by the SIFT-MS software for online calculations of the concentrations.²⁴ The kinetics library can be optimized to avoid overlaps (see Results and Discussion) or cross sensitivity.²⁴

The accuracy of the SIFT-MS analysis of volatile Se compounds is influenced by the same factors as previously described for SIFT-MS quantification of other volatile compounds from the ratio of the ion count rates: the reaction time, the rate constant, and the sample flow rate.²³ These parameters are determined for a given instrument with combined accuracy of $\pm 20\%$. Note that concentration of simultaneously quantified water vapor acts as a useful indicator of accuracy of measurement.^{28,29} The precision and reproducibility of the quantification is chiefly given by the counting statistics and is routinely calculated by the data analysis software.²³

Experiments demonstrating the feasibility of SIFT-MS quantification of volatile Se compounds released from maize plants (*Zea mays*) cultivated with an enhanced supply of Se nutrients were carried out by the following protocol: five different concentrations (0.2, 2.0, 10.0, 20.0, and 200 μM in aqueous solution) of selenium salts (sodium selenate, A, and sodium selenite, B) were used as a germinating medium to ascertain whether there is a correlation between the amounts and form of selenium salts and the amounts of volatile selenium compounds released by the seedlings. Ten Petri dishes were filled up with cotton-wool soaked with 5 mL of the different solutions. After 2 days, the maize seedlings grew to a length of about 3 cm and the characteristic garlic odor of $(\text{CH}_3)_2\text{Se}$ became noticeable. The headspace above the covered cultivating Petri dishes was analyzed using SIFT-MS in real time. Each sample was heated for 15 min at the temperature of 40 °C. A heated calibrated capillary was inserted inside the covered dish, and the concentration of $(\text{CH}_3)_2\text{Se}$ was measured using the multi-ion monitoring (MIM) mode;²³ the absolute

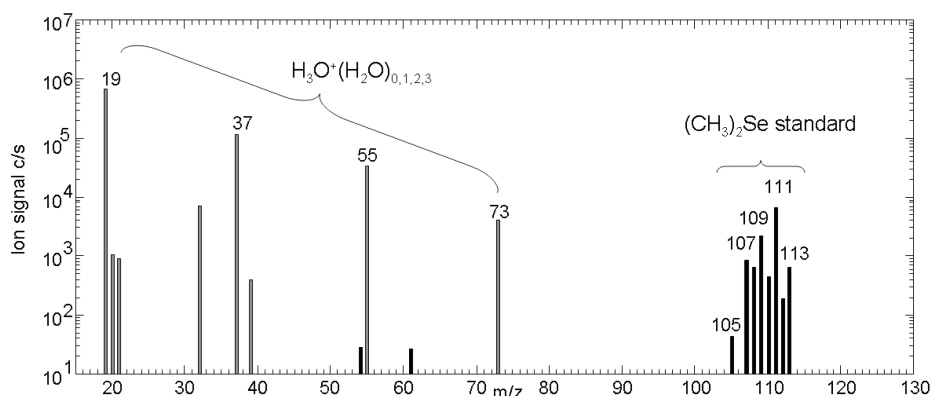


Figure 1. Mass spectrum obtained from the headspace of $(\text{CH}_3)_2\text{Se}$ standard mixture by averaging 12 consequential scans. Signals at m/z 112 and 114 are due to the lower resolution of quadrupole mass spectrometer and due to ^{13}C isotopologues. Minor signal at m/z 50 is $\text{O}_2^+\text{H}_2\text{O}$;²⁹ m/z 54 and 61 are presumably noise.

concentration was obtained. Thus, the headspace within the covered dish was collected directly, and ambient air was allowed to replace the depleted volume. Background concentrations of volatile Se compounds in the laboratory air were monitored before and after analysis of each sample and compared with the headspace concentrations.

Safety Considerations. The volatile reference reagent, dimethylselenide ($(\text{CH}_3)_2\text{Se}$), is toxic by inhalation, is toxic if swallowed, and causes danger of cumulative effects. This reagent must be handled with caution according to established laboratory safety practices using safety glasses and gloves for personal protection while ensuring good ventilation. Hydrogen selenide (H_2Se) was not used as a reagent, but it is one of the volatile compounds released by plants. H_2Se is also very toxic by inhalation, highly flammable, toxic in contact with skin, and potentially fatal even at low ppm levels. However, in the experiments described in this Article, the concentrations of H_2Se released by plants are seen to be much lower.

RESULTS AND DISCUSSION

Ion Chemistry of $(\text{CH}_3)_2\text{Se}$. The ion chemistry of the three precursor ions (H_3O^+ , NO^+ , and $\text{O}_2^{+\bullet}$) with the standard mixture of $(\text{CH}_3)_2\text{Se}$ was studied experimentally using the well established SIFT method for the determination of ion–molecule kinetics.²⁴ The reaction of H_3O^+ with $(\text{CH}_3)_2\text{Se}$ (Figure 1) produces the protonated ion $(\text{CH}_3)_2\text{SeH}^+$ exclusively, and its four major isotopologues appear at mass-to-charge ratios, m/z , of 107, 108, 109, 111, and 113. This is because selenium has five major stable isotopes: ^{76}Se (9.02%), ^{77}Se (7.63%), ^{78}Se (23.52%), ^{80}Se (49.82%), and ^{82}Se (9.19%) (the sixth isotope ^{74}Se has natural abundance less than 1%). This characteristic isotopic composition is very useful, because it can confirm the presence of Se in volatile compounds released by plants. Note that, unlike many protonated polar molecules, $(\text{CH}_3)_2\text{SeH}^+$ ions do not associate with water molecules forming hydrated ions. This means that the concentration of $(\text{CH}_3)_2\text{Se}$ in the sampled air can be calculated directly from the ratio of the product ion count rates to the precursor ion count rates without the need to consider formation of hydrates.²³

NO^+ and $\text{O}_2^{+\bullet}$ precursor ions were both observed to react with $(\text{CH}_3)_2\text{Se}$ (IE = 8.40 eV) via charge transfer without any fragmentation producing $(\text{CH}_3)_2\text{Se}^+$ at m/z 106, 107, 108, 110, and 112. The calculated values of the collisional rate constant (k_c) for the H_3O^+ reaction and the experimentally

derived rate constants (k) for the NO^+ and $\text{O}_2^{+\bullet}$ reactions are summarized in Table 1.

Ion Chemistry of H_2Se , CH_3SeH , $(\text{CH}_3)_2\text{Se}_2$. Following our previous experience with hydrogen sulfide (H_2S)³⁰ reactions, we presume that H_3O^+ will transfer a proton to H_2Se (proton affinity, PA, 707.8 kJ/mol)³¹ because Se has similar chemical properties to sulfur. Fragmentation after proton transfer cannot occur in this proton transfer reaction because the energy released (calculated as 16.8 kJ/mol from the PA of H_2O of 691 kJ/mol)³¹ is substantially smaller than the strength of the Se–H covalent bond. Thus, a nondissociative proton transfer occurring at the collisional rate²⁵ can be used for absolute quantification of H_2Se . The product ions H_3Se^+ at m/z 79, 81, 83, and 85 are used in the present study; however, there is a potential overlap with the second hydrate of protonated ethanol at m/z 83 and 85. NO^+ cannot react with H_2Se by an exothermic binary reaction because of the value of its ionization energy (IE H_2Se = 9.89 eV) that is larger than recombination energy of NO^+ (RE NO^+ = 9.2 eV). The reaction of $\text{O}_2^{+\bullet}$ is known from previous work³² to form the H_2Se^+ ion product that cannot be used for SIFT-MS analysis because it disappears completely from the flow tube due to its reaction with water to form H_3O^+ .

Methylselenol, CH_3SeH , is expected to have a higher PA than water on the basis of its structure (by analogy with the value of PA of methanethiol, CH_3SH , which is 773.4 kJ/mol), and thus, it will react with H_3O^+ via proton transfer forming $\text{CH}_3\text{SeH}_2^+$ (m/z 93, 95, 97, and 99). The value of the ionization energy of CH_3SeH is not available in the literature, but again by analogy with CH_3SH (IE = 9.44 eV), it is unlikely to react with NO^+ . We can only speculate that methylselenol will react with $\text{O}_2^{+\bullet}$ precursor ion by charge transfer followed by fragmentation. However, as it will be shown later, Se-enriched plants did not produce any methylselenol anyway, because it was not observed on the H_3O^+ SIFT-MS spectra. Similarly, dimethyldiselenide ($\text{C}_2\text{H}_6\text{Se}_2$, IE 8.1 eV) is expected to react with H_3O^+ forming the protonated molecule that would be present at a wide range of isotopologues (significant peaks ranging from m/z 185 to 193 with a characteristic distribution corresponding to two Se atoms). NO^+ and $\text{O}_2^{+\bullet}$ will react with $\text{C}_2\text{H}_6\text{Se}_2$ by charge transfer producing ions in the range from m/z 184 to 192. Again, later it will be shown that these characteristic product ions were not observed in the experiments with plants.

Measurement of Vapor Concentrations of Volatile Se-Compounds Released by Plants. Air above maize seedlings cultivated with an enriched supply of Se was analyzed by SIFT-MS, as described in the Experimental Section. SIFT-MS spectra were acquired while the heated calibrated capillary was inserted into the covered cultivation dishes. The detailed inspection of the full scan mass spectra obtained using H_3O^+ precursors (Figure 2) showed the presence of $(\text{CH}_3)_2\text{Se}$ and H_2Se but did

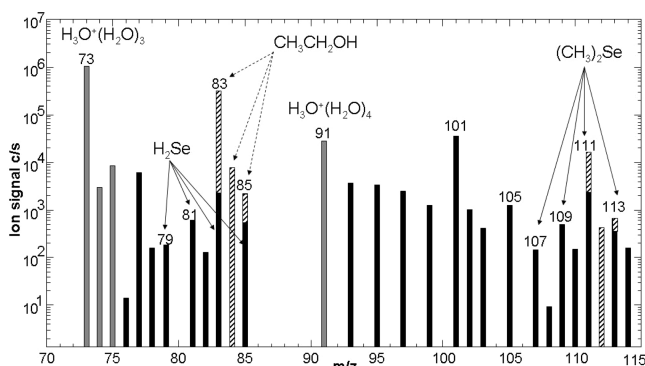


Figure 2. SIFT-MS mass spectrum obtained using H_3O^+ precursors while sampling air above maize seedling cultivated on Se-enriched medium. Note the characteristic product ions of $(\text{CH}_3)_2\text{Se}$ on the m/z 107, 109, 111, 113, and H_2Se in the mass range of m/z 79–85. The contribution of the overlapping ethanol product ions ($\text{C}_2\text{H}_5\text{OH}_2^+(\text{H}_2\text{O})_2$ at m/z 83, ^{13}C isotopologues at m/z 84, ^{18}O at m/z 85, and similarly $(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+\text{H}_2\text{O}$ at m/z 111, 112, and 113) are shown in the spectrum with a dashed pattern.

not indicate the presence of any of the other two possible volatile Se-compounds. Identification and also quantification of H_2Se can be complicated by overlaps with the second hydrate of protonated ethanol.^{38,39} However, presence of other isotopes allows its detection. Thus, the apparent isotopic ratios of H_3Se^+ differ from the expected and have to be corrected by subtracting the contributions from isotopologues of $\text{C}_2\text{H}_5\text{OH}_2^+(\text{H}_2\text{O})_2$. Similarly, the observed isotopic ratios for protonated $(\text{CH}_3)_2\text{Se}$ differ somewhat from the expected values, because of the overlaps of the isotopologues of $(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+\text{H}_2\text{O}$ at m/z 111. The headspace was also analyzed using a standard SPME/GC/MS method (mentioned in the introduction and described in detail in ref 16) to supplement the SIFT-MS results. These analyses confirmed presence of $(\text{CH}_3)_2\text{Se}$; however, as expected, H_2Se was not seen, due to the inability of SPME/GC/MS to detect such highly volatile molecules.

$(\text{CH}_3)_2\text{Se}$ was quantified in real time using the MIM mode for SIFT-MS analysis. The kinetics library used for quantification was thus constructed to calculate the absolute concentration of $(\text{CH}_3)_2\text{Se}$ from the ion signals at m/z 107 and 109 multiplied by a coefficient of 3 (corresponding approximately to the contribution of isotopologues $1/(0.0902 + 0.2352)$) to avoid contribution of the overlapping signal of ethanol. Sample results observed for $(\text{CH}_3)_2\text{Se}$ above cultivations with two different concentrations of two different Se salts are shown in Figure 3. This experiment indicated that SIFT-MS quantification of $(\text{CH}_3)_2\text{Se}$ is possible even at absolute humidity of the headspace air >7% corresponding to saturated water vapor pressure at temperatures in the range of 40–42 °C. The reproducibility of measurement was better than $\pm 3\%$ and was found to be limited by the counting statistics.²⁸

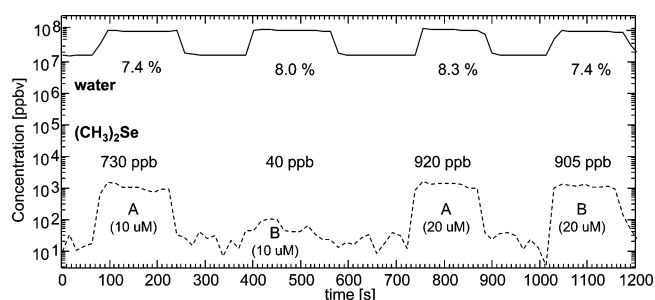


Figure 3. Time profile of concentration of $(\text{CH}_3)_2\text{Se}$ obtained using H_3O^+ precursors when the cultivation headspace is sequentially introduced into the SIFT-MS sample inlet from above seeds sprouting in four different media indicated (two different concentrations of sodium selenate, A, and sodium selenite, B; samples were heated at 40 °C). Concentration of water vapor by volume (absolute humidity calculated from the ion signals of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{1,2,3}$ ²⁸) is indicated by the solid line; the dashed line corresponds to the concentration of $(\text{CH}_3)_2\text{Se}$.

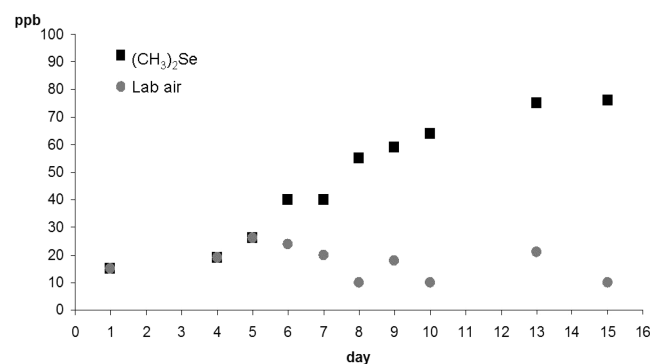


Figure 4. Time profile of the increasing concentration of $(\text{CH}_3)_2\text{Se}$ inside the Petri dish in comparison with the concentration in the background laboratory air.

Note that such reproducibility of quantification is typical for SIFT-MS measurements⁴⁰ of concentrations around 1000 ppb. These results indicate that the released volume of volatile $(\text{CH}_3)_2\text{Se}$ changes with the amounts and type of the selenium salt; however, the exact nature of this relationship, including details of saturation kinetics, will have to be established in more systematic experiments. Another open question is whether the observed $(\text{CH}_3)_2\text{Se}$ and H_2Se originate from the maize seedlings or from the bacterial activity within the growth medium inside the Petri dishes.

In order to demonstrate reproducibility of the quantifications and the ability of SIFT-MS to quantify temporal changes in concentration, we have repeated the analyses using the same seedlings and observed an increase in concentration of $(\text{CH}_3)_2\text{Se}$ in real time during several days of cultivation. The resulting values, together with the concentrations measured in the ambient laboratory air, are plotted in Figure 4. These results conclusively confirm that the observed volatile selenium indeed originates from the prepared samples and not from any pollution from the laboratory air.

CONCLUSIONS

SIFT-MS allows immediate quantification of H_2Se , CH_3SeH , $(\text{CH}_3)_2\text{Se}$, and $(\text{CH}_3)_2\text{Se}_2$ present in humid air based on the values of rate constants obtained in the present study. The study of ion chemistry of $(\text{CH}_3)_2\text{Se}$ provided new experimental

data on the product ions of H_3O^+ , NO^+ , and $\text{O}_2^{+\bullet}$ reactions. The experiments using maize seedlings showed that, from these four compounds, only H_2Se and $(\text{CH}_3)_2\text{Se}$ are produced in measurable concentrations (>1 ppb) in the air adjacent to plants growing in Se-enriched medium. To our knowledge, these were the first online quantitative and selective measurements of concentrations of volatile Se compounds. There were also no indications on the SIFT-MS mass spectra of the presence of selenoformaldehyde, H_2CSe , or diallyl selenide, $(\text{C}_3\text{H}_5)_2\text{Se}$, that were not included formally in the present study. Further experiments now can be done in order to fully utilize the potential of the SIFT-MS analytical method described in this Article. The first questions that need answering is how much volatilization of Se is realized by bacteria in soil or on the plant roots and how much conversion of inorganic Se to organic Se compounds occurs within the plants. In order to answer this question, we intend to perform similar experiments using defined bacterial cultures and to analyze emissions from the plant leaves separately from the soil in which the plants are growing.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We would like to thank Kseniya Dryahina for assistance with some of the SIFT-MS experiments and David Smith for reading and correcting the manuscript. We gratefully acknowledge financial support by the Grant Agency of the Czech Republic (project 203/09/0256) and by Grant Agency of Charles University (project GAUK 32010).

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