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Atmospheric sampling Townsend discharge ionization mass spectrometry for analysis of gas-phase mixtures

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Abstract

Atmospheric sampling Townsend discharge ionization (ASTDI) mass spectra of 65 different volatile organic compounds within 12 different functional groups have been evaluated. The sample air was introduced directly into the reduced pressure Townsend ion source by means of a deactivated capillary. The positive ion ASTDI mass spectrum of dry background air was dominated by the two precursor ions, $O_2^{\bullet+}$ (100%) and NO^+ (30%). Hydride abstraction, proton transfer, charge exchange and NO^+ addition produced mass spectra with detailed fragmentation useful for structural elucidation. Quasi-molecular ions (e.g., $[M+H]^+$) and adducts ions (e.g., $[M+NO]^+$) indicated the molecular weight for nearly all the investigated compounds. H_3O^+ emerged in the background spectrum of humid sample air, which produced, e.g., $[M+H]^+$ from hydrogen transfer for most oxygenated compounds. By dilution of the sample air with methane prior to the Townsend source, $O_2^{\bullet+}$ was depleted and $C_2H_5^+$ became the most intense reagent ion. This favored formation of $[M+H]^+$, whereas NO adduct ions diminished in the resulting ASTDI(Me) spectra. Identification of the molar weight and functional group was possible, since each functional group exhibited a unique combination of quasi-molecular and NO^+ adduct ions.

Keywords: Townsend discharge ionization; Chemical ionization; Atmospheric sampling

1. Introduction

On-line techniques are particular convenient for the study of reaction products from oxidation of biogenic volatile organic compounds (VOCs). The development of these techniques has advanced significantly over the past years, and they do not suffer from the same inherent disadvantages as off-line techniques do [1]. Fourier transformed infrared spectroscopy (FTIR), for example, is widely used in reaction chamber and flow reactor studies [2,3], although the carbonyl region of the spectrum may not be specific for quantifying single components. Mass spectrometry has been utilized for on-line analysis of gaseous mixtures such as VOCs and automobile exhaust. For example, proton transfer reaction-mass spectrometry (PTR-MS) has been used to measure reaction products of VOCs and ozone with detection limits in the parts per trillion (ppt) range [4,5]. Organic compounds are ionized by $(H_2O)_nH_3O^+$ clusters, which are also the reagent ions in atmospheric pressure ionization (API-MS). Use of the MS/MS mode with collision activated dissociation allows the products ion spectrum of a given ion peak, which is observed in the MS scanning mode, to be obtained [6]. Atmospheric sampling glow discharge ionization (ASGDI) has been used for determination of trace organics in ambient air [7], and monoterpene oxidation products of which multifunctional products could be differentiated by use of MS/MS [1]. Organic compounds in air is sampled into the ASGDI source and ionized in a plasma of $O_2^{\bullet+}$, NO^+, NO_2^+ and H_3O^+ reagent ions, the relative abundances depends on the glow discharge current [7]. Ionization occurs through various pathways including electron ionization, electron capture and ion–molecule reactions with the reagent ions, and the resulting mass spectra can be complex [8]. Except for NO_2^+, the reaction mechanisms and kinetics of the reagent ions above have been thoroughly studied by the group of Smith and Spanel [9]. They used a selected-ion flow tube (SIFT) MS for real-time analysis of trace gasses in air. NO^+ is also the reagent ion in nitric oxide chemical ionization (NOCI), which is a powerful technique for structure elucidation of a

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number of functional groups [10–18]. NO^+ is formed from NO supplied to the ion source at ca. 1 Torr, and reacts by hydride abstraction, charge exchange or addition. The importance of these products depends strongly on the functional group and the NO pressure. NO is, however, a strong oxidizing gas, which in its pure form deteriorates the filament in ion sources [10]. Over the years modified NOCI applications with diluted NO reagent gas have been developed, which improve the lifetime of the filament [17,19,20]. Alternatively, the filament can be replaced by a Townsend discharge ionization source, which is unaffected by pure or diluted oxidizing gasses [21].

Here we evaluate atmospheric sampling Townsend discharge ionization (ASTDI) MS of 65 different VOCs within 12 different functional groups under dry and humid conditions, either undiluted or mixed with methane reagent gas. As with ASGDI, organic compounds in air is sampled into the reduced pressure ASTDI source and ionized in a plasma dominated by $O_2^{\bullet +} > NO^+ > NO_2^+ > H_3O^+$ reagent ions. However, Townsend discharge applies a higher potential difference than glow discharge, and the resulting current is lower, 10^{-9} to 10^{-6} A [21,22]. To the best of our knowledge, the application of a Townsend discharge to an air/VOC mixture has not been described previously.

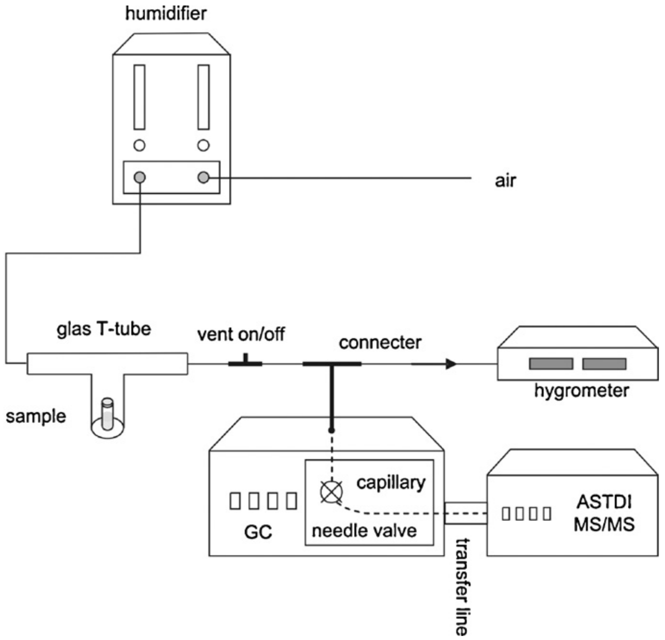

Fig. 1. The experimental set-up of atmospheric sampling Townsend discharge ionization mass spectrometry (ASTDI). The vapor of volatile organic compounds in air was sampled directly into the Townsend discharge source through a deactivated capillary.

2. Experimental

2.1. Instruments

A Varian 1200L triple quadrupole mass spectrometer was equipped with a Townsend discharge source (Varian, CA) operated in the positive mode. A controlled flow of volatile organic compounds was generated by evaporation of a pure standard in a vial situated in the lower leg of a glass T-tube (see Fig. 1). The vapor was diluted with dry/humid clean air (1–2 ppm toluene equivalents) and connected to a 1/4 in. stainless steel T-connection. The lower exit was connected to a needle valve in a heated GC (Varian CP 3800, CA). A 0.53 mm uncoated/deactivated capillary (Varian ME-05-14-1, CA) connected the needle valve to the Townsend discharge source through the GC and transfer line (both 100 °C). The sample flow was adjusted to 6 ml/min. The ion counts at a particular mass/charge ratio (*m/z*) increased with the Townsend discharge voltage (500–2000 V) and reached a plateau. A total of 1600 V was applied in this study. The source temperature was 100 °C, in favor of thermo labile compounds, and the formation of structurally characteristic ions [23,24]. On the other hand, a too low source temperature could cause additional peaks in the higher mass region, which arises from dimerization followed by fragmentation [25]. A discharge in dry air appeared at a source pressure of ca. 0.3 Torr, which produced mainly $O_2^{\bullet +}$ and NO^+ (Fig. 2a). The data in Tables 1–5 were obtained at 0.4 Torr, at which the ion count of a toluene molecular ion (250 ppb) was highest. The standard scan range was *m/z* 50–300 at a scan time of 1.0 s, and 20 spectra were averaged. With these settings a signal-to-noise ratio of S/N = 3 was determined by online ASTDI sampling of 3 ppb toluene (*m/z* 92). The concentration of the standards (Tables 1–4) were measured using a calibrated photo ionization detector (RAE systems, CA) with an accuracy of ±20 ppb or 10% of reading.

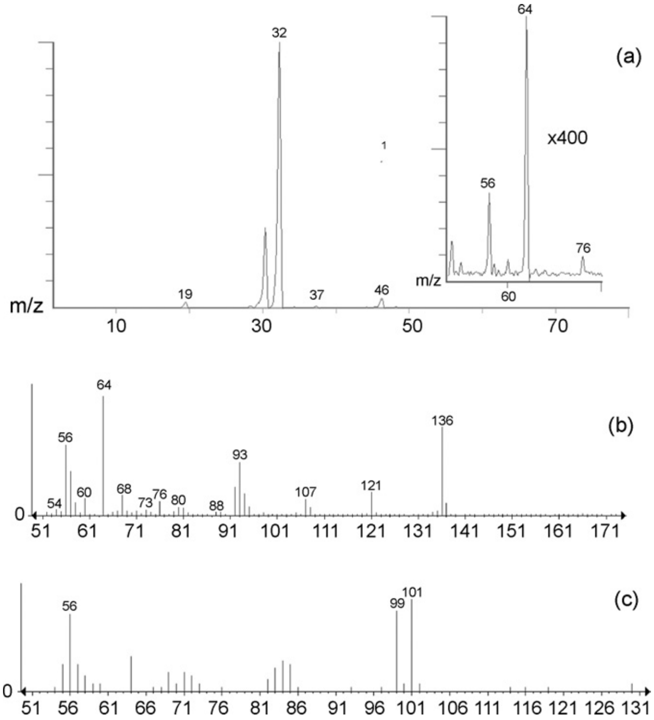

Fig. 2. ASTDI spectrum of dry (a) clean air; (b) D-limonene; (c) 1-hexanol.

Table 1
Abundances of selected ions for some hydrocarbons in ASTDI, compared with NOCI and *SIFT MS* precursor ions (H_3O^+, $O_2^{\bullet+}$ or NO^+)

Selected ions	$[M-OH]^+$	$[M-3H]^+$	$[M-2H]^+$	$[M-H]^+$	M^+	$[M+H]^+$	$[M+2H]^+$	$[M-2H+NO]^+$	$[M+NO]^+$
Alkanes [10,25,28,30]		NOCI		NOCI $O_2^{\bullet+}$, NO^+	$O_2^{\bullet+}$			NOCI	
Octane			3	34	41	2			
Decane			2	100	45	10			1
Cyclohexane				26	100	6			
Substituted benzenes [15,30]				NOCI	NOCI $O_2^{\bullet+}$, NO^+	H_3O^+			NOCI
Toluene				10	100	30			1
Alkenes [14,21,24,27,28,31]				NOCI NO^+	NOCI $O_2^{\bullet+}$, NO^+	H_3O^+			NOCI NO^+
1-Hexene	5	3	2	27	100	11	93		42
1-Heptene	4	8	6	20	90	8	54		50
1-Nonene		7	6	10	82	18	4	4	100
Cyclohexene		2		24	100	9			2
4-Vinyl cyclohexene	4			20	100	12			5
α-Pinene	8		5		45	6			
D-Limonene	6		5	5	100	10	1	1	
α-Terpinene	100		65	7	76	10			
1-Octen-3-ol	38		3	22	6		5	10	

Table 2
Abundances of selected ions for some oxygenated compounds in ASTDI, compared with NOCI and *SIFT MS* precursor ions (H_3O^+, $O_2^{\bullet+}$ or NO^+)

Selected ions	$[M-OH]^+$	$[M-3H]^+$	$[M-2H]^+$	$[M-H]^+$	M^+	$[M+H]^+$	$[M+2H]^+$	$[M-2H+NO]^+$	$[M+NO]^+$
1° alcohols [16,32,33,34]	H_3O^+ $O_2^{\bullet+}$	NOCI		NOCI $O_2^{\bullet+}$, O^+	$O_2^{\bullet+}$, NO^+	H_3O^+		NOCI	NOCI
1-Butanol	65	95	55	60	5		10	15	
1-Hexanol	35	71	7	95	6			13	
1-Heptanol	20	74	10	100	13	2		14	
2° alcohols [16,32,34]	NOCI H_3O^+ NO^+, $O_2^{\bullet+}$			NOCI NO^+		H_3O^+		NOCI	
2-Heptanol	58	8	32	100	12	2		79	
3-Heptanol	42	6	38	82	11			70	
Cyclopentanol	24		100	84	45	2		55	
3° alcohols [16,32]	NOCI								
t-Amylalcohol	100	2	9		60	1	1	6	
t-Butanol	43								
Ethers [32,35]				NOCI NO^+		H_3O^+			
Dibutyl ether				81	15	2	5		
1,2-Diethoxy-ethane				73	22	3			
2-Butoxyethanol	5	34	5	69	14			3	
Diethylene glycol	2			97	14	6			5
Dimethyl ether									
Epoxides [28,36]	H_3O^+			NOCI	$O_2^{\bullet+}$, NO^+	H_3O^+			NOCI
Limonene-1,2-epoxide				8	24	3			4
α-Pinene oxide				8	24	5	2	2	5
Cyclohexene oxide	100	2	1	10	41	100	8	3	3
Hydroperoxides [37]									
tert-Butyl hydroperoxide	6		94	6	1				
Cumene hydroperoxide					2				

Table 3
Abundances of selected ions for some carboxylic compounds in ASTDI, compared with NOCI and *SIFT MS* precursor ions (H_3O^+, $O_2^{\bullet +}$ or NO^+)

Selected ions	$[M-OH]^+$	$[M-2H]^+$	$[M-H]^+$	M^+	$[M+H]^+$	$[M+2H]^+$	$[M-2H+NO]^+$	$[M+NO]^+$
Aldehydes [17,32,38,39]	H_3O^+		NOCI					
			NO^+	O_2^+	H_3O^+			
Pentanal	4	3	100	12	3			1
3-Methylbutanal			100	15	1	5		1
Hexanal	4	5	100	10			2	3
Heptanal	2		100	16				
2-Pentenal			100	89	6	2		3
2-Heptenal			100	50	5	2		10
Glutaraldehyde	2	6	100	18	12			4
Ketones [17,39,40,33]					H_3O^+			NOCI
				NO^+, O_2^+				NO^+
3-Methyl-2-butanone		2	2	100	6	12	2	87
3-Hexanone				100	10	1		92
3-Heptanone				83	8	2		100
2,4-Dimethyl-3-pentanone		1		39	3		1	29
5-Methyl-2-hexanone		4	33	37	5	1		100
3-Methyl-5-heptanone		2	2	60	8	1	1	71
5-Nonanone				59	7	5		83
Cyclohexanone		2		100	8			55
Acetophenone				23	4			42
Carvone				40	6	10		100
4-Hydroxy-4-methyl-2-pentanone	63			5				15
Hydroxy-acetone	20	6	10	50	4	10	34	100
Carboxylic acids [18,32,41]	NOCI		NOCI	NOCI				NOCI
	H_3O^+				H_3O^+			
	NO^+			O_2^+				NO^+
Butanoic acid	28	3	2	28	8	2	8	100
Pentanoic acid	40	2	12	7	8	1	25	42
Hexanoic acid	48	5	9	26	7	2	28	100
Esters [18,32,41]								NOCI
					H_3O^+			NO^+
Butyl acetate			12	5	5			100
Methyl butyrate				5	2			25
Butyl butyrate				2	2	1		57
Ethyl-2-methyl butyrate			1	11	1			26
Methyl pentanoate			3	5	3			26
i-Butyl acrylate			16	3	2			100
t-Butyl acetate								
t-Butyl acrylate				2				

2.2. ASTDI

Essentially two major precursor ions were present in the background mass spectrum of clean sample air, NO^+ (30%) and $O_2^{\bullet +}$ (100%). Traces of NO_2^+ (2%) were also observed (Fig. 2a). At higher ion source pressures the NO_2^+/NO^+ ratio increased, which altered the mass spectra of, e.g., nitro compounds to include $[M+NO_2]^+$. Moreover, the $O_2^{\bullet +}$ peak diminished, and

Table 4
Abundances of selected ions for some nitro compounds in ASTDI, compared with NOCI and *SIFT MS* precursor ions (H_3O^+, $O_2^{\bullet +}$ or NO^+)

Selected ions	$[M-NO_2]^+$	$[M-OH]^+$	$[M-3H]^+$	$[M-2H]^+$	$[M-H]^+$	M^+	$[M+H]^+$	$[M+2H]^+$	$[M-2H+NO]^+$	$[M+NO]^+$
Nitro compounds [42]	H_3O^+						H_3O^+			
	O_2^+									NO^+
Nitroethane							1			100
2-Nitropropane							16			100
Nitrobenzene						100	10			36
5-Nitro-1-pentene		7			7	9	2			100
2-Nitro-1-propanol		5	9	2	20	2	7		28	100

Table 5
Selected ions characteristic for some functional groups in ASTDI(Me)

Selected ions	$[M-OH]^+$	$[M-H]^{+a}$	$[M+H]^{+a}$	$[M+H_2O]^{+b}$
Alkanes		Abundant quasi-molecular ion		
Benzenes			Abundant quasi-molecular ion	Present
Alkenes			Abundant quasi-molecular ion	
Alcohols[c]	Base peak	Abundant quasi-molecular ion		Present
Ethers			Abundant quasi-molecular ion	Present
Epoxides	Base peak		Abundant quasi-molecular ion	Present
Hydroperoxides				
Aldehydes	Present		Abundant quasi-molecular ion	Present
Ketones			Abundant quasi-molecular ion	Present
Carboxylic acids	Present		Abundant quasi-molecular ion	Present
Esters			Abundant quasi-molecular ion	Present
Nitro compounds			Abundant quasi-molecular ion	Present

[a] Quasi-molecular ions were always more abundant than M^+.
[b] *tertiary*-Amylalcohol did not form $[M+H_2O]^+$.
[c] $[M-H]^+$ was not observed for tertiary alcohols.

the total reagent ion count decreased. Other ions were minor, but they covered the *m*/*z* range 19–76 and were therefore considered during interpretation of unknown spectra. For example, H_3O^+ (*m*/*z* 19) and clusters hereof, $NO^{\bullet+}H_2O$ (*m*/*z* 48), $N_2^{\bullet+}$ (*m*/*z* 28), $N_2^{\bullet}N_2^{\bullet+}$ (*m*/*z* 56), $NO^{\bullet}NO^+$ (*m*/*z* 60), $(O_2)_2^{\bullet+}$ (*m*/*z* 64) and $NO_2^{\bullet}NO^+$ (*m*/*z* 76). ASTDI mass spectra of humid air samples differed from those of dry air (see later).

2.3. ASTDI(Me)

Mass spectra were recorded by mixing the sample air with methane (dilution 1:8), prior to the Townsend source. A source pressure was kept at 4 Torr, where the D-limonene $[M+H]^+$ ion was observed to be most intense. The ion current was an order of magnitude greater than in ASTDI, and the background mass spectrum of dry air appeared more complex. Although the relative abundance of NO^+ and $O_2^{\bullet+}$ was significant, other ions accounted for more than 75% of the total ion count. The base peak was $C_2H_5^+$, and the peak pattern did not change at 20% RH.

2.4. Chemicals

The chemicals in Table 1 were purchased from Acros, Aldrich, Fisher, Fluka, Lancaster Synthesis, Merck and Sigma in purity greater than 95% and used without further purification. Clean dry air was prepared from compressed outdoor air, which was double charcoal filtered corresponding to medical grade. NO_2 (4.95 ± 0.01 ppm in N_2) was from Hydrogas, Norway.

3. Results and discussion

3.1. ASTDI mass spectra

The ASTDI mass spectra resembled those of NOCI and related techniques such as CH_3NO_2 CI [20,25], N_2O CI [26] and NO/H_2 CI [19], in which NO^+ is a major precursor ion. However, ASTDI mass spectra provided abundant molecular or quasi-molecular ions, and detailed fragmentation from ion–molecule reactions with $O_2^{\bullet+}$ and NO^+ precursor ions. NO_2^+ was only present in a few percent abundance, and not likely to influence the ion chemistry (Fig. 2a). Examples of ASTDI mass spectra are illustrated in Fig. 2b (limonene) and c (1-hexanol). Note the molecular ion of 1-hexanol (*m*/*z* 102) and the abundant quasi-molecular ions $[M-3H]^+$ and $[M-H]^+$. H_3O^+ was present in humid air samples, but minor (0.03%) in dry air samples. Ion–molecule reactions, and ion–product ion reactions proceeded according to the individual rate constant and abundances of each precursor ion. $O_2^{\bullet+}$ reacts with most VOCs, as indicated by its ionization energy (EI), which is greater than most VOCs (12.1 eV). Non-dissociative charge transfer produces M^+ ions, and dissociative charge-transfer results in two or several fragment ions [9]. EI of NO^+ (9.3 eV) is lower than $O_2^{\bullet+}$, and only one or two product ions are typically formed during reaction with NO^+. These are $M^{\bullet+}$ (charge transfer), $[M-H]^+$ (hydride ion transfer), $[M-OH]^+$ (hydroxide ion transfer), $[M-OR]^+$ (alkoxide ion transfer) and $[M+NO]^+$ (adduct or ion–molecule association) [9]. Product ion distributions and rate constants of H_3O^+, $O_2^{\bullet+}$ and NO^+ with numerous organic compounds have been reported using SIFT MS (see references in Tables 1–4).

Tables 1–4 serve to compare the formation of selected ions (e.g., M^+) in ASTDI with NOCI and individual precursor ions in SIFT MS (H_3O^+, $O_2^{\bullet+}$ or NO^+). Relative abundances of the selected ions are listed for 65 organic compounds within 12 functional groups. Within each functional group, it is stated which selected ions are characteristic for NOCI and SIFT MS. The dry sample conditions imply that the precursor ions are essentially $O_2^{\bullet+}$ and NO^+ (NO_2^+ is ca. 2%). The ions should be indicative of the molecular mass and functional group. Comparison of these ions formed in ASTDI with those formed in NOCI and SIFT MS is possible within each functional group. For example, terminal alkenes were characterized by abundant $[M+NO]^+$ in all three techniques [14,15,27] that increased with chain length. Only selected ions typical for a given functional group are included in Tables 1–5 (references to the original NOCI and SIFT MS studies are included in the tables). NO^+ is a common precursor ion in all three techniques, but the product ions are not identical. Some characteristic ion are unique for NOCI, e.g., formation of $[M-3H]^+$ and $[M-2H+NO]^+$ for alkanes, the latter of which is believed to include a long-lived collision complex of an alkane, NO^+ and NO [10]. At some points ASTDI resembled NOCI more than SIFT MS. A characteristic $[M-3H]^+$ ion was observed in the spectrum of 1° alcohols, and $[M-2H+NO]^+$ ions in the spectra of 1° and 2° alcohols. Since none of these ions are observed for 3° alcohols, ASTDI is capable of differentiating between isomeric alcohols, which is also the case for NOCI [16]. The position of the epoxide functional group can be located by use of MS/MS, because an abundant acylium ion is formed by cleavage of the epoxide [28]. Aldehydes and ketones, which are structural isomers, are easily differentiated by all three techniques. In many cases, however, the occurrence of characteristic ions in ASTDI can be predicted from the knowledge of the individual precursor ions obtained by SIFT MS. For example, alkanes react with H_3O^+ by proton transfer if the proton affinity (PA) of the hydrocarbon is larger than that of H_2O ($691\,kJ\,mol^{-1}$). For the reactions of $O_2^{\bullet+}$ and NO^+, charge transfer and dissociative charge transfer is expected, when the ionization potential (IP) of the hydrocarbon is smaller than that of the reagent ions [29]. However, as more than one precursor ion is present simultaneously, the importance of a particular ion–molecule reaction is influenced by the rate constant and the abundance of the particular precursor ion. Consequently, adducts such as $[M+NO]^+$ are typically less abundant as opposite to molecular/quasi-molecular ion formed by $O_2^{\bullet+}$. Ions corresponding to 12 and 14 mass units above the molecular ion were observed in minor abundance, albeit up to 16% abundance for 2-butoxyethanol and other ethers. These may be secondary product ions, the identity of $[M+12]^+$ probably being $[M-H_2O+NO]$.

The combination of characteristic ions appears to be unique for a particular functional group, as shown in the data in Tables 1–5. An M^+ base peak suggests an alkene. The presence of an additional major $[M+NO]^+$ peak suggests a ketones, or terminal alkene if a $[M-H]^+$ is also observed. Mass spectra of carboxylic acids include both $[M-2H+NO]^+$ and $[M+NO]^+$. ASTDI spectra of esters included an abundant $[M+NO]^+$, whereas others peaks related to the molecular mass were of low abundance. Exceptions were *tertiary*-butyl esters absent of peaks indicative of structural information or molecular mass. $[M+NO]^+$ was the base peak of nitro compounds and for nitroethane no other characteristic ions were available. However, mono-substituted nitro compounds were easily recognized by their uneven mass. The characteristic ions of alkanes, substituted benzenes and internal alkenes are fairly similar in ASTDI, but unique ions are encountered in ASTDI(Me) (see later; Table 5). The same is true for aldehydes and ethers, which are easy to differentiate in humid air samples (see later). The unique combination of characteristic ions for a particular functional group is a powerful property of ASTDI/ASTDI(Me), unlike techniques which uses one precursor ion at the time like PTR-MS and SIFT MS.

Real-time analysis of monoterpene oxidation products using glow discharge ionization has recently been reported [1]. The sample ionization occurred in the glow discharge regime, while the present study used Townsend discharge, which is characterized by a smaller degree of ion and free electron production [22]. Glow discharge and Townsend discharge produced background spectra with the same precursor ions, albeit in different intensities [7]. However, glow discharge mass spectra of, e.g., D-limonene looks very different from that of Townsend discharge, which provide detailed fragmentation and resembles the EI mass spectrum (Fig. 2b).

3.2. ASTDI(Me) mass spectra

These differed from the ASTDI spectra at some important points (Table 5). A quasi-molecular ion, either $[M-H]^+$ or $[M+H]^+$, was always more abundant than M^+. However, $[M-H]^+$ was only observed for alkanes, 1° and 2° alcohols. $[M+H_2O]^+$ was observed for most organic compounds, and an abundant $[M-OH]^+$ characterized alcohols, epoxides and carboxylic acids. The ASTDI mass spectrum alone, was often insufficient for identification of unknowns, because the identity of the peak at the highest *m*/*z* value is not known. Unless the mass spectral data is ascribed to molecular ion/quasi-molecular ions and/or adduct ions, molecular weight and functional group cannot be deduced. For example, a ketone was easily identified, since the mass spectrum included two abundant ions, M^+ and $[M+NO]^+$, the *m*/*z* difference being equal to the mass of NO. The same numerical difference could be observed for carboxylic acids, but their spectra included $[M-2H+NO]^+$ as well. Terminal alkenes included $[M+2H]^+$ in addition to $[M-H]^+$ and $[M+H]^+$ of significant abundance. Esters which included $[M+NO]^+$ as the only significant ion was difficult to identify, and functional groups attached to *tertiary*-alkyl groups often provided little structural information, if any. Generally, a determination of the molecular mass was possible. A qualified guess based on the peak pattern in ASTDI could be verified by inspection of the ASTDI(Me) spectrum for the occurrence of $[M+H_2O]^+$ and a quasi-molecular ion (Table 5). Moreover, abundant NO^+ adducts in the ASTDI spectrum should be markedly reduced in ASTDI(Me), due to the lowered abundance of this precursor ion.

3.3. The effect of relative humidity

Sampling at 20% RH produced a background with a higher H_3O^+ signal and minor abundance of clusters thereof. H_3O^+ functions as a Brønsted acid in the gas phase and protonates most organic compounds resulting in stable $[M+H]^+$ ions. As H_3O^+ becomes more abundant it competes with $O_2^{\bullet+}$ and NO^+ in ion–molecule reactions. Molecular or quasi-molecular ions becomes more abundant at the cost of fragmentation. ASTDI of humid air samples and SIFT MS shared many similarities [9], because the precursor ions were the same (NO_2^+ being of minor importance). Not all organic species were sensitive to an increase of the ambient H_2O content. Largely unaffected functional groups were hydroperoxides and alkanes, even though formation of H_3O^+ adducts of alkanes has been reported in a SIFT MS study [30]. Appearance (or increase) of $[M+H]^+$ was observed for ketones, alkenes, ethers and the epoxides. The dry and humid air spectra of alcohols were dominated by $[M-3H]^+$ and $[M-H]^+$, but $[M-H+H_2O]^+$ appeared in the humid air samples, except for 3° alcohols. $[M-H+H_2O]^+$ is ascribed to association of a H_2O molecule with the product ion ($[M-H]^+$) of NO^+ and the alcohol [9]. The remainder of the fragmentation pattern was largely unchanged. $[M+H]^+$ and $[M+H+H_2O]^+$ were observed in the humid air spectrum of aldehydes, carboxylic acids and nitro compounds. The latter results from association of H_2O molecules with the protonated molecule [9], and was of minor abundance in the spectrum of the dialdehyde glutaraldehyde. $[M+NO]^+$ was among the most abundant peaks in the mass spectra of esters, and this did not change in humid air samples. The presence of H_2O, however, made $[M+H]^+$ more abundant than $[M-H]^+$ as opposed to dry air samples.

ASTDI(Me) of humid air samples differed slightly from dry air samples for some compounds. In the humid air spectra of aldehydes and nitro compounds, $[M+H+H_2O]^+$ increased at the cost of $[M+C_2H_5]^+$. The abundance of $[M-H]^+$, M^+, $[M+H]^+$ and $[M+H_2O]^+$ did not change, and thus H_2O vapor did not disturb the assignment of the molecular mass.

4. Conclusion

ASTDI is a soft ionization technique for on-line identification of VOC mixtures in air.

Only two precursor ions ($O_2^{\bullet+}$ and NO^+) are essentially present in dry sample air, and the spectra typically differed from NOCI by less abundant or absence of NO^+ adducts. M^+ and fragment ions were more abundant in ASTDI, due to fast charge exchange by $O_2^{\bullet+}$ ion–molecule reactions in the Townsend source. The ability of NOCI to differentiate 1°, 2° and 3° alcohols, and ketones and aldehydes applied to ASTDI as well. However, *tertiary*-butyl substituted esters and stable *tertiary*-hydroperoxides were not easily identified. Generally, the combination of ASTDI and ASTDI(Me) at variable RH enabled determination of the molecular mass. Identification of the functional group was also possible in most cases, since each functional groups exhibited a unique combination of quasi-molecular and NO^+ adduct ions in ASTDI and ASTDI(Me). The presence of additional functional groups appeared to add on to these characteristics.

It appears that the versatility of precursor ions allowed ASTDI to differentiate between functional groups, which is an advantage over the more sensitive PTR-MS technique. In principle ASTDI corresponds to SIFT MS using two or three (depending on RH) precursor ions simultaneously, in an air matrix instead of He in the SIFT flow tube. Observed differences in the mass spectre could be explained by secondary reactions between product ions and other precursor ions, or matrix effects. SIFT MS has an advantage over ASTDI in producing simple spectra excellent for quantification purposes. The advantage of ASTDI appears to be qualitative in terms of identification of unknown organic compounds.

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