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Microwave plasma ion sources for selected ion flow tube mass spectrometry: Optimizing their performance and detection limits for trace gas analysis

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We dedicate this paper to the memory of Sharon Lias in recognition of her major contributions to ion thermochemistry that have greatly assisted us and many others in ion chemistry research.

Abstract

The performance of the ion sources used in selected ion flow tube mass spectrometry, SIFT-MS, instruments is paramount in determining their sensitivities and detection limits for trace gas analysis. The microwave discharge plasma ion source that is currently used for the production of currents of the precursor H_3O^+, NO^+ and $O_2{}^+$ ions for SIFT-MS is described, and the ion chemistry occurring within the plasma and the dissociation of the precursor ions on the helium carrier gas are considered. Thus, it is shown that the most suitable ion source gas composition is a mixture comprising maximal water vapour and minimal air at the lowest total pressure at which the discharge is sustained and stable. It is also shown that the injection energies of the precursor ions into the helium carrier gas must be kept low to minimize collisional dissociation of the ions and thus to minimize the fraction of reactive impurity ions in the carrier gas. Under these conditions, count rates greater than $10^6\ s^{-1}$ of all three precursor ion species with less than 1% of impurity ions have been achieved, which has moved the detection limit of SIFT-MS analyses of the volatile metabolites present in exhaled breath and ambient air into the 0.1–1 parts-per-billion concentration regime.

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Keywords: Microwave plasma ion source; Selected ion flow tube mass spectrometry; SIFT-MS; Breath analysis; Volatile organic compound

1. Introduction

Selected ion flow tube mass spectrometry, SIFT-MS, exploits chemical ionisation of the trace gases in air/breath samples by mass selected precursor ions, viz., H_3O^+, NO^+ or $O_2{}^+$, under truly thermal conditions. The ion thermochemistry (so thoroughly researched and compiled by Lias et al. [1]) indicates, as required, that these precursor ions do not react with the major components of air (N_2, O_2, CO_2, and Ar), react with H_2O vapour only slowly but do react with most organic and inorganic breath metabolites. SIFT-MS has proven to be a valuable addition to the techniques available for trace gas analysis of ambient air and exhaled breath [2,3]. The precursor ion species are formed in an ion source and separately injected upstream into fast-flowing helium carrier gas where they react with the trace gases in the sample that has been introduced downstream at a known flow rate. The reactions generate product ions that are characteristic of the particular trace gases present and the currents (in practice count rates) of these product ions and those of the precursor ions are detected by a downstream mass spectrometer thus facilitating trace gas analysis. More will be said about this later, where it will be explained that the currents of mass selected precursor ions that are injection into the carrier gas, and thus the count rates of these ions at the downstream mass spectrometer/detection system, determine the sensitivity of this analytical method. It is for this reason that much effort has been applied to the development and choice of ion sources for SIFT-MS.

This paper is concerned with the optimization of the microwave ion sources currently used for SIFT-MS, and

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the concomitant improvement in the sensitivity of SIFT-MS analytical technique.

2. Ion sources for SIFT-MS

SIFT-MS essentially is an extension of the selected ion flow tube, SIFT, technique, which was developed for the study of ion–molecule reactions in the gas phase [4]. Various types of ion source were used in this application, including low pressure electron ionisation ion sources [5], higher pressure Nier-type sources [6] and flowing afterglow ion sources [7,8]. These gave acceptable precursor ion count rates of a wide variety of ions, which allowed wide-ranging studies of ion–molecule reactions [5,9]. These sources require specific source gases to generate the required ions and the first two types need electron emitting filaments that have shorter lifetimes than desirable when corrosive source gases such as moist air have to be used. Hence, for SIFT-MS we choose to use a microwave cavity discharge through moist air [10] to generate the H_3O^+, NO^+ and $O_2{}^+$ precursor ions.

These microwave discharges are established in a glass tube separated from the upstream mass filter by a disc D_1 in which there is a central orifice O_1 that is small enough to allow pressures approaching 1 Torr to be established in the ion source whilst ensuring that the pressure in the mass filter is maintained at about 10^{-4} Torr by a turbomolecular pump (Fig. 1). A mixture of ions formed in the discharge is extracted through O_1 (typically 1 mm diameter) and focused into the mass filter. The ion species of the chosen mass-to-charge ratio, m/z, then fall onto another disc D_2 that forms part of a Venturi-type gas injector with a central orifice O_2 through which a fraction of the ions pass and enter the helium carrier gas. The ions are convected down the flow tube to yet another disc D_3 with a central orifice O_3, which samples the ions from the carrier gas into the analytical quadrupole mass spectrometer. The currents of ions are measured on both discs D_2 (typically 1–100 nA) and D_3 (typically 1–100 pA), these being valuable parameters for instrument setup and control, as will be seen later.

The first SIFT-MS microwave ion sources consisted of an Evenson cavity coupled to a large laboratory power supply by a long transmission line cable. Much of the early SIFT-MS work was carried out with this arrangement, but tuning of the cavity to reduce reflected power could be tricky. This prompted us to consider a new design in which a rectangular cavity is coupled to a low power magnetron [11], thus eliminating the power cable. The magnetron is powered by a small supply located close to the cavity/magnetron arrangement. The glass tube in which the discharge is created is inserted through the cavity, as is shown in Fig. 1. This arrangement, which requires no tuning skills, is now used in the smaller generation of transportable SIFT-MS instruments (*Profile 3* used for this study, manufactured and supplied by Instrument Science Limited, Crewe, UK).

In using these ion sources it is clear that the gas mixture, specifically the humidity of the air source gas and the total pressure, critically determines the total ion currents and the relative signals of the three precursor ion species. To date, in the development of the SIFT-MS analytical method, we have made little effort to improve the efficiency of these sources, but now with the drive towards greater sensitivity of the new smaller SIFT-MS instruments, it has become important to obtain a better understanding of their operation in order to increase the current levels of the three precursor ions. Thus, we have undertaken a systematic study of the behaviour of these sources. This is the subject matter of this paper. It will be shown how greater ion signal levels have been obtained and how this has moved the detection limit for trace gas analysis in breath and air by SIFT-MS towards partial pressures in the 100 parts-per-trillion regime.

3. Experimental approach

The commercial instrument for SIFT-MS (*Profile 3*, Instrument Science Limited, Crewe, UK) has been adapted to include two separate needle valves allowing the precise control of the composition of the ion source gas. The experimental approach to the ion source optimization was to systematically vary the

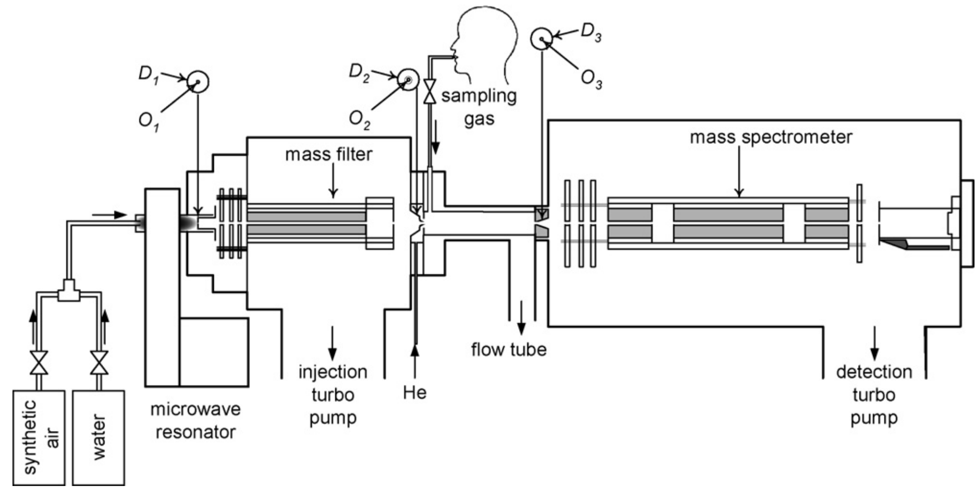

Fig. 1. A schematic diagram of the *Profile 3* SIFT-MS instrument used for this study. The *D* and *O* symbols refer to the ion collection discs and the ion transit orifices, respectively.

following ion source variables: the total pressure of air plus water vapour in the ion source, p_t, the partial pressures of dry (synthetic) air, p_a, the partial pressure of water vapour, p_w, and the power dissipated in the microwave discharge, whilst using the mass filter in combination with the D_2 current to separate the precursor ions and measure their levels. The microwave discharge became somewhat unstable at p_t lower than 0.5 Torr and so this was the lowest p_t for these experiments, even though the experimental data presented below indicate that some small increase of the ion currents could be available at lower pressures. Also, the microwave power was varied within the limits of the stability of the discharge, but no appreciable effect was observed on the composition of the ions produced. Thus, the magnetron high voltage power supply was stabilised to provide 50 W for all these experiments.

3.1. *Influence of the source gas composition*

The potentials on the electrostatic lenses that focus the ions into the quadrupole mass filter and into O_2 in D_2 (see Fig. 1) were optimized for maximum ion current measured at D_2 and then the individual ion currents at *m*/*z* values 19 (H_3O^+), 30 (NO^+) and 32 (O_2^+) were measured (see the results in Fig. 2) as p_t, p_a and p_w were varied in the ion source. This indicated the currents of each ion species emerging from the source, allowing the source gas variables to be adjusted to enhance the currents of the three ion species, as required.

3.2. *Influence of the ion injection energy*

The next operation is to optimize the currents of the ions flowing through O_2, since ultimately this is the important parameter that maximises the precursor ion currents reaching D_3. The precursor ion count rates as recorded by the ion detector/electron multiplier (see Fig. 1) are then directly proportional to the currents passing through O_3 and the analytical mass spectrometer. The ion current injected into the flow tube through O_2 depends to some extent on the laboratory energy, E_i, of the ions arriving at D_2 (which is held close to ground potential), but if this is too high then the impact energy of the ions on the helium atoms of the carrier gas, i.e., the centre-of-mass energy, E_{cm}, can result in partial dissociation of the precursor ions to produce more reactive fragment ions (see Section 4.2). The reactions of these ions with the common air and breath species N_2, O_2 and H_2O (always present in very high concentrations compared to the trace gases to be analysed) can produce "impurity precursor ions" in the carrier gas, resulting in the appearance of undesirable product ions via their reactions with sample trace gases, which unduly complicate the analyses. This phenomenon is especially obvious for the more fragile H_3O^+ precursor ions, as we will show. The unwanted ion chemistry involved will be discussed briefly in Section 4. Thus, the E_i must be suitably low and this is achieved by reducing the potential of D_1 to a suitable value (see Fig. 1). Data are presented below that show the variation of the "impurity ion" production with E_i, which allow the appropriate E_i to be established to minimize the fractions of the impurity ions in the carrier gas.

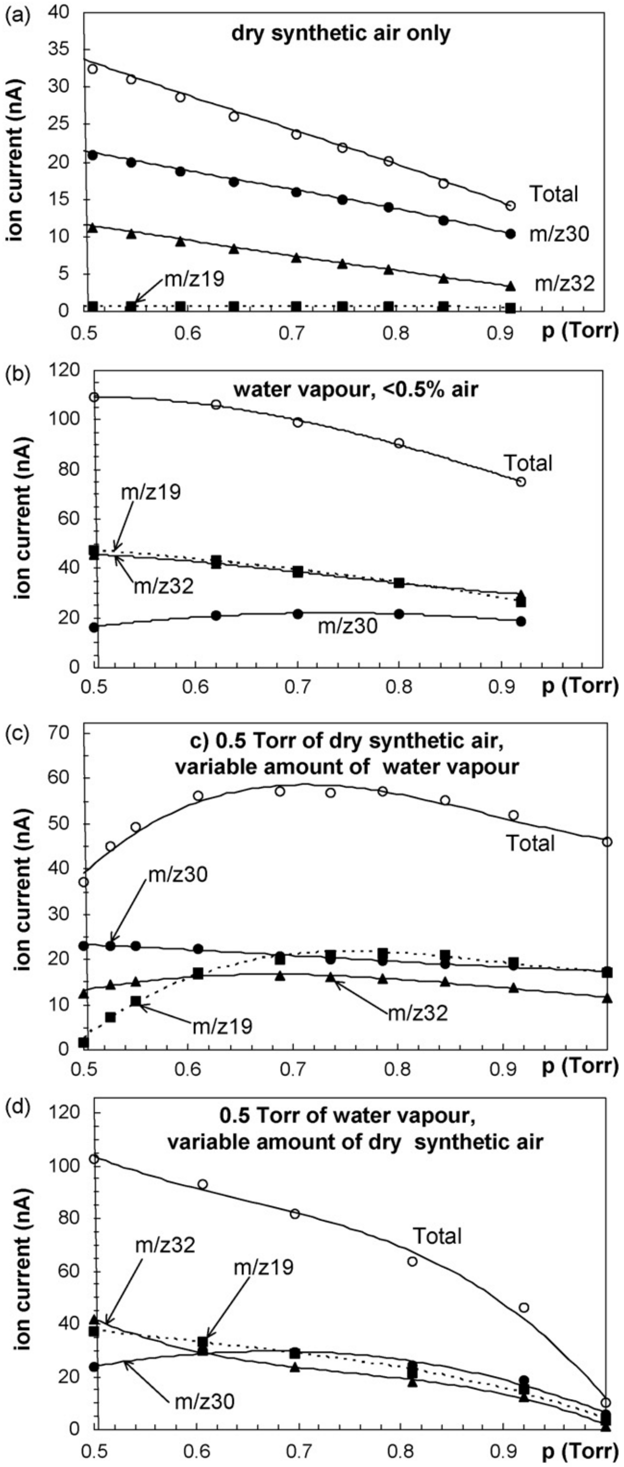

Fig. 2. The currents of ions at *m*/*z* values 19 (H_3O^+), 30 (NO^+) and 32 (O_2^+) and the total ion current collected by disc D_2 (see Fig. 1) as the total source gas pressure is varied over the range indicated. The currents are derived from the amplitudes of the ion current peaks obtained when the mass filter is used as a scanning mass spectrometer.

4. Results and discussion

In this section, we first describe the currents of individual ions generated by the ion source as the source gas mixture is varied, explaining the observations in terms of the ion chemistries that occur. Then we discuss the observed collision induced dissociation of the three precursor ions as they enter the carrier gas, as seen through the "impurity ions" detected by the downstream mass spectrometer analytical system. Finally, we present sample SIFT-MS full scan spectra [2] obtained in the current optimized *Profile 3* instrument and note the detection limits that are realised using the current microwave ion source.

4.1. Ion currents and ion source gas components

The currents of H_3O^+, NO^+ and $O_2{}^+$ ions, as measured at D_2, for four distinguishable gas mixture situations, ranging over total pressures, p_t, from 0.5 Torr to 1.0 Torr, are shown in Fig. 2 for (a) dry synthetic air only, (b) water vapour only with <0.5% air, (c) synthetic dry air at a fixed pressure of 0.5 Torr with variable additional amounts of water vapour, and (d) water vapour at a fixed pressure of 0.5 Torr with variable additional amount of dry synthetic air. The E_i of the precursor ions impacting on D_2 is 16 eV, as determined by the potential difference between D_1 and D_2.

The first obvious trend seen throughout the data is that increasing pressure generally results in a decreasing total ion current; in Fig. 2c a small maximum in the total current is observed. This can be explained by a reduced current flow from the plasma to D_1 at the higher pressures; the observed maximum as the water content is increased is due to the increased ionisation efficiency of water vapour compared to that for air (N_2 and O_2) and the reduced diffusive loss of ions and electrons from the plasma to the glass walls (where recombination efficiently occurs). The effect of increasing pressure is even more marked in the results of the experiment shown in Fig. 2d where the total ion current drops to 10 nA when the total pressure is increased to 1 Torr and at even higher pressures the signal rapidly disappears. At the total pressure of 1 Torr the value of the total ion signal is very sensitive to even small changes in the source gas composition and thus the results from the experiments (c) and (d) do not exactly match at the highest pressure even though the nominal composition of the mixture in each case is 0.5 Torr of air and 0.5 Torr of water vapour.

The appearance of a small current of H_3O^+ (<1% of the total ion current) ostensibly from the discharge through dry air illustrates the difficulty of removing all water vapour from the system. The H_3O^+ is formed in the fast reactions of H_2O molecules with the OH^+, H_2O^+, N^+ and O^+ ions that are formed by direct dissociative ionisation of H_2O, N_2 and O_2 molecules, thus

$$OH^+ + H_2O \rightarrow H_3O^+ + O \quad (1)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (2)$$

$$N^+ + H_2O \rightarrow H_2O^+ + N \qquad \text{(then reaction (2))} \quad (3)$$

$$O^+ + H_2O \rightarrow H_2O^+ + O \qquad \text{(then reaction (2))} \quad (4)$$

The NO^+ formed in these plasmas, in which there is minimal neutral NO, is due to the reactions of the O^+ and N^+ atomic ions formed in the discharge with N_2 and O_2 molecules, thus

$$O^+ + N_2 \rightarrow NO^+ + N \quad (5)$$

$$N^+ + O_2 \rightarrow NO^+ + O \quad (6)$$

The $O_2{}^+$ is formed via direct ionisation of O_2 molecules and via the reaction of O^+ and H_2O^+ ions with O_2 molecules, thus

$$O^+ + O_2 \rightarrow O_2{}^+ + O \quad (7)$$

$$H_2O^+ + O_2 \rightarrow O_2{}^+ + H_2O \quad (8)$$

Clearly, the efficiencies of non-dissociative and dissociative ionisation of the N_2, O_2 and H_2O neutral components by plasma electrons and the speed of the above ion–molecule reactions will determine the relative currents of the three required precursor ions emerging from the discharge plasma. Detailed modelling of these parameters could be carried out, but this is not the objective of this work, which is the practical realisation of an efficient source of the required precursor ions.

It is inconvenient to have to change ion source parameters during the use of SIFT-MS instruments; rather it is simplest to maintain a set mixture of water vapour and air at a fixed pressure. The above experiments have shown that for this microwave discharge arrangement it is best to fix p_t at the lowest workable value of about 0.5 Torr at which the discharge is stable. The data shown in Fig. 3 show how the total ion current and the currents of H_3O^+, NO^+ and $O_2{}^+$ ions emerging from the source vary as the percentage of air is increased (and hence as the percentage of water vapour is decreased) whilst maintaining p_t constant at 0.5 Torr. Clearly, the total current is greatest when the source contains largely water vapour (Fig. 3a), but the NO^+ current is at a minimum (Fig. 3b), as might be expected since ion–molecule reactions involving neutral N_2 molecules and N^+ ions form this precursor ion (see reactions (5) and (6)). What mixture of water vapour/air is used is a matter of judgement as to which precursor ion should be at the highest count rate for SIFT-MS analyses. It is clear from numerous studies that H_3O^+ and NO^+ ions are the most versatile and thus optimization of the source parameters to ensure the largest signals of these two ions is desirable, whilst ensuring a workable signal of $O_2{}^+$ ions. Inspection of the data in Fig. 3 shows that a good compromise is a source gas mixture consisting of a few percent air at which the total currents of the ions emerging from the source has been reduced by only a few percent. It is also seen that for this mixture the $O_2{}^+$ ion current is also comparable with the currents for the other two precursor ions. As mentioned above, these currents reflect the count rates of these precursor ions available for SIFT-MS analyses.

4.2. Dissociation of injected ions

It is obviously desirable in SIFT-MS that the chosen precursor ions should be the only ions present in the helium carrier gas. This requires perfect filtering of the ions in the injection quadrupole (Fig. 1) and no dissociation of the chosen ions in their collisions with the helium carrier gas atoms, as described in Section 3.2. In practice, the filtering of the three precursor

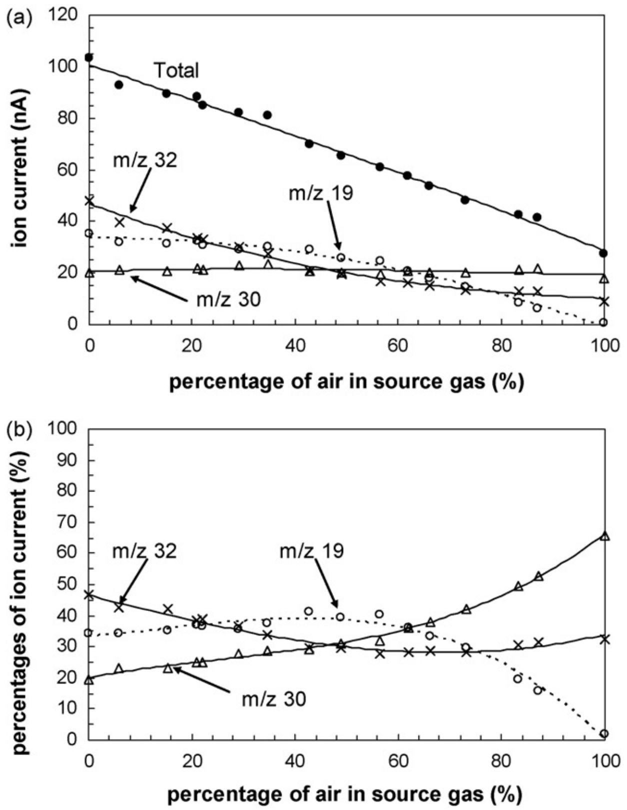

Fig. 3. (a) The currents of ions at *m/z* values 19 (H_3O^+), 30 (NO^+) and 32 (O_2^+) and the total ion current collected by disc D_2 as the fraction of dry air and water vapour are varied at a fixed total pressure of 0.5 Torr. (b) The current for each ion species from (a) expressed as percentages. These percentages are quite reproducible even between different instruments, unlike the absolute currents that are influenced by multiple factors.

ions is effectively perfect (better than 0.05% O_2^+ when injecting NO^+ and vice versa). However, collisional dissociation cannot be eliminated completely but easily minimized. Shown in Fig. 4 are the percentages of the three precursor ions and the related “impurity ions” present in the carrier gas, as measured using the downstream mass spectrometer detection system (Fig. 1) as each precursor ion species is injected separately into the helium/air sample gas mixture whilst the laboratory energy, E_i, is varied. As the potential of D_1 is changed to vary E_i, the potentials of the other electrodes in the ion focusing array and the potential of the quadrupole axis were also changed in sympathy to maintain the optimum focusing condition.

Consider the injection of H_3O^+ ions and thus the data shown in Fig. 4a. Note that as E_i, and hence E_{cm}, is increased above about 20 eV, the percentage of H_3O^+ decreases and that of O_2^+ increases and a trace of NO^+ appears. This is the result of the partial dissociation of the H_3O^+ ions in collision with helium atoms producing H_2O^+ ions that react with O_2 molecules producing O_2^+ ions according to reaction (8). The threshold E_i of 20 eV for the production of the reactive ion fragments (and thus of O_2^+) corresponds to an E_{cm} of 3.47 eV. The O–H bond dissociation energy in H_3O^+ is 6.2 eV according to the data from Ref. [1], this means that more than one collision is involved in dissociation of H_3O^+ ions near the threshold E_i.

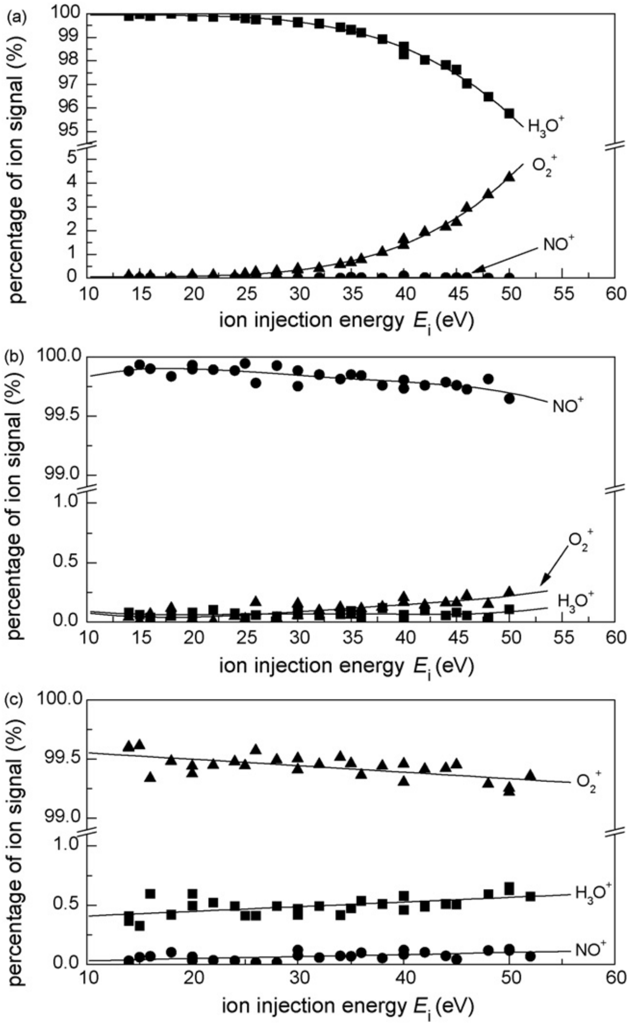

Fig. 4. Percentages of the ion count rates registered at the analytical mass spectrometer as a function of the ion injection energy, E_i, for (a) H_3O^+, (b) NO^+ and (c) O_2^+ ions. Note that the *y*-axis is broken to show the percentages of the injected (major) ions as well as those of the “impurity” (minor) ions.

Now consider the injection of NO^+ ions and the data shown in Fig. 4b. The more strongly bound NO^+ ions dissociate only a little producing O^+ and N^+ ions, which react with O_2 and H_2O molecules via reactions (3), (4) and (7) producing the observed small amounts of O_2^+ and H_3O^+ ions. The small amounts of the O_2^+ ions can also be explained by vibrational or electronic excitation of the NO^+ ions on their collision with He atoms followed by charge transfer to O_2.

O_2^+ also partially dissociates to O^+ ions, which react with H_2O and N_2 molecules via reactions (4) and (5) producing H_3O^+ and NO^+ ions, respectively, as indicated in the data given in Fig. 4c. Vibrationally excited O_2^+ can also charge transfer to H_2O ultimately producing H_3O^+ in reaction (2). The data indicate that the fraction of any vibrationally excited O_2^+ ions is less than 1%.

The inference to be drawn from these data is that for optimum purity of each precursor ion in the helium carrier gas, the E_i should be as low as possible consistent with an acceptable ion currents into the carrier gas. In practice, an E_i in the range

15–20 eV is suitable at which the currents of the ions has not decreased by more than 20% below that attainable at higher E_i values.

4.3. Implications to SIFT-MS analyses: sample spectra

Following the above guidelines regarding the source gas content and pressure and the injection energies of the selected ions, together with careful optimization of the currents injected into the flow tube via orifice O_2 by adjustment of the potentials on the post-filter focusing electrodes (see Fig. 1), currents of the mass selected precursor ions arriving at D_2 are typically within the range 10–50 nA for source pressures within the range 0.50–0.75 Torr and for E_i of 15–20 eV. Because of the necessity to prevent unacceptable back flow of the helium carrier gas into the injection quadrupole mass filter chamber, which would raise

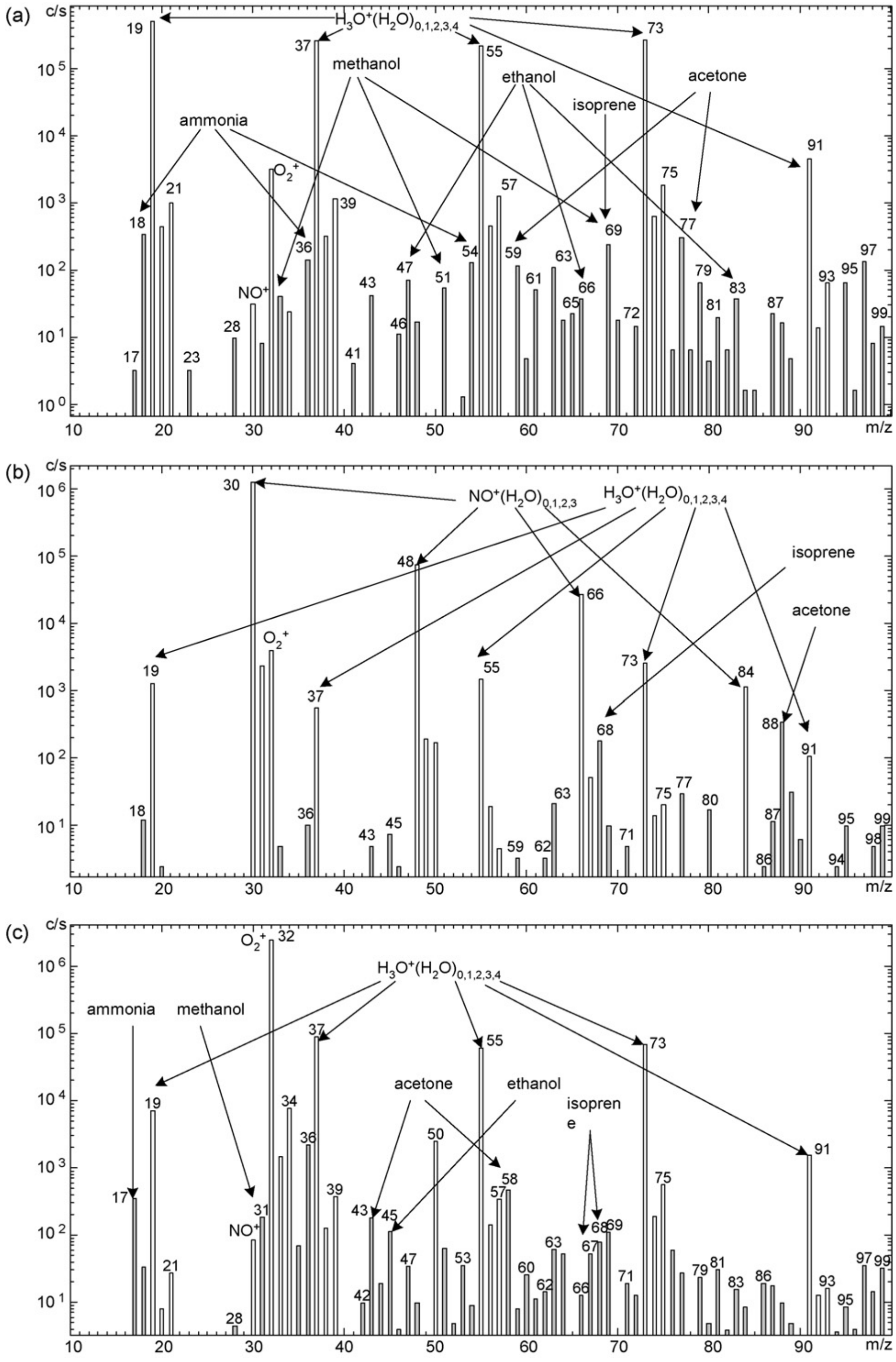

Fig. 5. SIFT-MS spectra using (a) H_3O^+, (b) NO^+ and (c) $O_2{}^+$ ions, given as ion counts per second, c/s, as a function of the ion mass-to-charge ratio, *m/z*, obtained as exhaled human breath enters the helium carrier gas. The open vertical peaks indicate the precursor ions and their isotopic variants, and the filled peaks are the product ions that indicate the presence of the trace gas metabolites in the breath sample.

the pressure to levels that would diminish the performance of the mass filter, the diameter of O_2 must be suitably small. For the size of turbomolecular pump used to evacuate the mass filter chamber (255 l/s pumping speed on the current *Profile 3* instrument) the diameter of O_2 is 0.7 mm. This inevitably reduces the currents flowing into the carrier gas below the nA currents arriving at D_2 (see Fig. 1). At the helium carrier gas pressure used in *Profile 3* (in the range 1.0–1.5 Torr), the current arriving at the downstream D_3 sampling disc is typically within the range 10–50 pA. The fraction of this ion current flowing through the orifice O_3, and hence the c/s of ions at the detection system, obviously depends on the diameter of this orifice. For the *Profile 3* range of instruments, O_3 can be chosen as 0.3, 0.4 or 0.5 mm, depending on the pumping speed of the pump maintaining the low pressure in the analytical quadrupole chamber against the loading of the carrier gas, the larger the diameter the greater being the c/s and the better the analytical sensitivity of the instrument (see below). In the present instrument, O_3 has a diameter of 0.3 mm and this translates into precursor ion count rates of typically 10^6 counts per second, c/s, as can be seen in Fig. 5, which is a montage of three SIFT-MS spectra obtained as a breath sample flows into the carrier gas and the analytical mass spectrometer is scanned over the range of mass-to-charge ratio, *m*/*z*, from 10 to 100 for each of the three precursor ions.

As can be seen in these spectra, the fractions of injected "impurity ions" are small in accordance with an E_i used of 15 eV and they indicate that the fraction of the vibrationally excited NO^+ ions is less then 1%. Product ions appear that are characteristic of the major trace gases in exhaled breath, as indicated, including ammonia, acetone, methanol, ethanol and isoprene. Details of the ion chemistries and the identification of these compounds have been given in several previous papers [2–4] and their level distributions within the general population are reported in several recent papers [12–16], so these are not presented here. However, relevant to this paper are the sensitivity and the detection limits achieved with the current SIFT-MS instruments after the optimization of the ion source and the resulting increase in the precursor ion count rates.

The concentration of a particular compound in an air/breath sample, as obtained using SIFT-MS, depends on several parameters, including the sample flow rate, the rate coefficient of the reaction of the precursor ion with the particular trace gas, the reaction time and the count rates of the product ions to those of the precursor ions (the count rate ratio). A general method for the calculation of absolute trace gas concentrations in air and breath from selected ion flow tube mass spectrometry data has been recently described and documented in this journal [17]. The larger is the precursor ion count rate the larger will be that of the product ions. Since in practice count rates as low as 1 c/s and lower can be faithfully recorded down to the background "noise" count rate (typically 0.1 c/s for the present instruments), then using the presently constructed ion source and in excess of 10^6 c/s of precursor ions, as described above, analytical count rate ratios of $>10^7$ can be realised. Taking into account the parameters involved in the calculation of the trace gas partial pressures as mentioned immediately above, and presented in detail in the major papers on SIFT-MS [2,17], real time analyses of 10 s breath exhalations for trace gases present at partial pressures within the range 0.1–1 ppb can be achieved. This now brings into the analytical range of SIFT-MS those known low level breath metabolites such as formaldehyde (a marker of tumours (Amann private communication)), acetaldehyde [16] (also likely to be released by tumours in vivo [18]), propanol (a potential indicator of diabetes [14]) and HCN (an indicator of pseudomonas lung infection [19]).

5. Concluding remarks

The understanding gained by the present study of the microwave ion sources now routinely used for SIFT-MS analyses has lowered the detection limit of the current instruments. These developments will continue moving more low level breath metabolites within the compass of SIFT-MS analysis. Improvements in ion source technology and a greater appreciation of the physics and ion chemistry involved will form an essential part of this continuing research and development programme.

Acknowledgements

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