The use of dopants in high field asymmetric waveform spectrometry†

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Ion mobility spectrometry (IMS) is proven core technology for the gas-phase detection of chemical warfare (CW) agents. One disadvantage of IMS technology is that ions of similar mobility cannot readily be resolved, resulting in false alarm responses and a loss of user confidence. High field asymmetric waveform spectrometry (HiFAWS) is an emerging technology for the gas-phase detection of CW agents. Of particular interest is the potential of a HiFAWS-based platform to reduce the number of false alarms by resolving ions that cannot be discriminated using IMS. It has been demonstrated that a water clustering/declustering mechanism can be a dominant process in HiFAWS. Ions that cannot be discriminated in IMS because they possess the same low field mobility value can be resolved using HiFAWS due to differences in the extent of low field ion solvation and high field ion desolvation. When operating in complex environments such as those potentially experienced in military and security arenas, IMS systems commonly employ internal dopants to reduce the number of background responses. It is possible that HiFAWS systems may also require the use of internal dopants for the same reason. It has been demonstrated that dopants employed for use in IMS may not be suitable for use in HiFAWS.

1. Introduction

1.1. Ion mobility spectrometry (IMS)

Ion mobility spectrometry (IMS) is proven core technology for the gas-phase detection of chemical warfare (CW) agents, explosives, narcotics and some toxic industrial chemicals. There are a relatively large number of IMS-based instruments commercially available for use in military and security arenas. Instruments are configured for specific applications and can vary considerably in size, shape, weight, power and internal temperature and chemistry.

The principles of IMS are well documented.[1–3] Typically, vapour-phase sample is drawn into the IMS inlet and ionised *via* an atmospheric pressure chemical ionisation (APCI) process. The resultant ions are driven by an electric field towards an electronic shutter. The shutter opens periodically allowing the ions to be injected into a drift region where the ions attain a characteristic and constant velocity (v_d) which is determined by several factors including the applied electric field (E), the cell temperature and pressure, the drift gas composition and flow rate and the properties of the ion (mass, shape, size, polarisability, *etc.*). The ion charge is detected at a Faraday plate collector with ions separated according to their mobility (K) in the drift region, where $K = v_d/E$.

One disadvantage of IMS technology is that ions of similar mobility cannot readily be resolved, resulting in false alarm responses and a loss of user confidence. When sampling in complex environments such as those experienced in military and security arenas, chemicals other than those of interest may be ionised to give an IMS response. These chemicals become 'interferents' when the product ions detected possess similar mobility values to the ions that the IMS system is programmed to detect, thereby giving rise to false positive alarms.

Finally, any CW agent detection system for use in the field is required to operate over a wide range of environmental conditions. Changes in atmospheric pressure, temperature and humidity can strongly influence the extent of low field water clustering which, in turn, can affect the low field ion mobility. A variety of approaches are used in IMS-based systems to minimise or monitor low field ion mobility changes arising as a consequence of changing environmental conditions. These include the use of suitable sampling inlets, *e.g.* membranes or pinholes, the recirculation of internal air through molecular sieve and the measurement of temperature and pressure within the IMS cell.

1.2. High field asymmetric waveform spectrometry (HiFAWS)

Typically, IMS systems operate under low field conditions ($E <$ 1000 V cm^{-1}) where the ion mobility is found to be independent of the electric field applied along the length of the cell. However, it is known that at high electric field strengths (*e.g.* $E >$ 10 000 V cm^{-1}) the mobility of an ion can change.[4] A technique referred to throughout this article as high field asymmetric waveform spectrometry (HiFAWS) can readily generate these high field strengths and exploits the fact that ions of similar low field mobility (K_l) may be differentiated owing to differences in mobility at high fields (K_h).

The first description of HiFAWS was published in the external literature in the early 1990s.[5,6] The technique, described in

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detail elsewhere,[5–8] requires the application of an rf waveform containing both a high field component and low field component (of opposite polarity) across a HiFAWS cell that may be of concentric cylinder[7] or parallel plate[8] design. The gap between the cylinders/plates is typically a few millimetres, enabling high fields to be obtained upon application of moderate voltages. HiFAWS is also referred to in the literature by a variety of synonyms such as field asymmetric ion mobility spectrometry (FAIMS), radio frequency ion mobility spectrometry (rf-IMS), field ion spectrometry (FIS) and differential mobility spectrometry (DMS).

In a HiFAWS system, vapour-phase sample is drawn into an ionisation region and ionised *via* APCI processes in a similar manner to that described for IMS. Ions are then transported by a carrier air stream from the ionisation region through the HiFAWS cell towards the Faraday plate collector. There is no requirement for an electronic shutter. An asymmetric waveform is applied across the HiFAWS cell, normal to the carrier air stream transporting the ions. This waveform is configured such that ions exhibiting no mobility dependence on the electric field ($K_h = K_l$) pass through the cell to the detector (provided that the rf frequency is sufficiently high to prevent ion destruction at the cell walls). At typical rf frequencies of 1 MHz, an ion may oscillate several thousand times as it travels through the HiFAWS cell before reaching the detector.

The technique is reliant upon the fact that the mobility of an ion can change as it rapidly oscillates between high field and low field conditions. A schematic diagram of ion motion in a HiFAWS cell is shown in Fig. 1. This particular example depicts two ions with identical low field behaviour (*i.e.* the ions would be indistinguishable in an IMS system) that can be discriminated due to differences in their behaviour at high fields. In the example shown, the high field mobility of one ion increases compared to its low field mobility value ($K_h/K_l > 1$), whereas in the case of the other ion, the high field mobility of the ion decreases compared to its low field mobility ($K_h/K_l < 1$). In order to detect the ions a dc voltage sweep can be superimposed on the rf waveform to compensate for ion drift towards the upper or lower plate. Ions are then detected at a characteristic compensation voltage (CV).

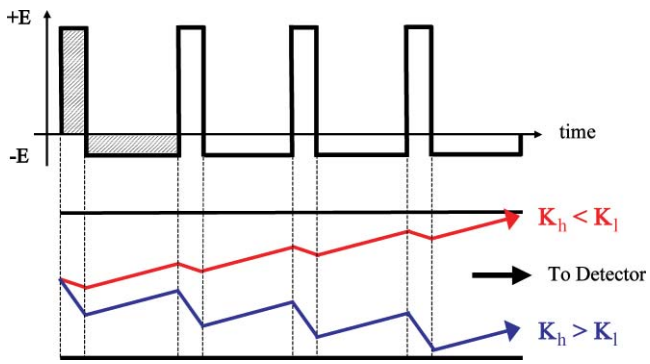

Fig. 1 Schematic diagram showing ion motion in HiFAWS (example shows separation of two ions with identical low field mobility value).

The ability of HiFAWS to resolve ions that cannot be readily discriminated by IMS has been demonstrated in the laboratory. Clearly, one of the principal potential advantages of a HiFAWS-based platform for CW agent detection and monitoring is to reduce false alarm rates. However, the demands on a detection system for use in the field are high and just as IMS systems require approaches to control or monitor low field ion mobility changes arising as a consequence of changing environmental conditions, so HiFAWS-based platforms are likely to require similar approaches for successful deployment in the field. IMS equipment often employs an internal dopant source in order to reduce the response from complex and unknown backgrounds. It is possible, for similar reasons, that a dopant source may be required in a HiFAWS system operating 'in the field'. Unfortunately, traditional dopants used in IMS appear to perform less well in HiFAWS. This paper describes work carried out at Dstl Porton Down and highlights problems associated with the use of traditional dopants in HiFAWS.

2. Experimental

A HiFAWS system supplied by Sionex Corporation, Bedford, USA (SVAC – Sionex Value Added Component) was used to obtain all topographic dispersion plots presented. These plots have been obtained using software developed at Sionex Corporation.

The interfacing of HiFAWS to a mass spectrometer allows confirmatory identification of the ions detected. As the SVAC system could not be readily interfaced to our laboratory mass spectrometers, two HiFAWS cells were constructed in-house and interfaced directly *via* 50 μm orifice plates to two separate quadrupole mass spectrometers: one tuned for external positive ions (SXP 600, VG Quadrupoles, UK) and one tuned for negative ions (SXP Elite, VG Quadrupoles, UK). The dimensions of the in-house HiFAWS cell and the HiFAWS cell employed in the Sionex SVAC were very similar. All trends observed on the Sionex SVAC could be reproduced on the in-house HiFAWS/mass spectrometers. The in-house HiFAWS cells contain no detector electrodes; thus, on application of the appropriate compensation voltage, ions pass directly through the cell and into the mass spectrometer *via* the pinhole orifice. Driving electronics for the in-house HiFAWS cells were supplied by Sionex Corporation.

The gas handling system used for all instruments is shown schematically in Fig. 2. Purified air supplied to the laboratory is further treated by passing air through sieve packs containing a mixture of 5A/13X molecular sieve. The bulk of the air stream (0–1 l min^{-1}) passes through a mass flow controller (MFC1). A second controller, MFC2 (0–50 ml min^{-1}) was connected to a water bubbler allowing water vapour to be delivered to the bulk air stream in a controlled and constant manner. The CW agent vapour generator is supplied with up to 2 l min^{-1} of purified air (again further purified by using sieve packs containing 5A/13X molecular sieve). The third controller, MFC3 (0–50 ml min^{-1}) delivers the CW agent vapour to the conditioned bulk air stream. At the dopant injection point, a syringe drive (Harvard Apparatus) is used to inject dopant headspace vapour into the air stream. All mass flow controllers are manufactured by MKS Instruments and are connected to an MKS four-channel readout. The water concentration of the bulk air stream is measured using an MCM Dewmatic (Moisture Control and Measurement, UK) and can be controlled and maintained at any water concentration between 2 and 1000 ppm.

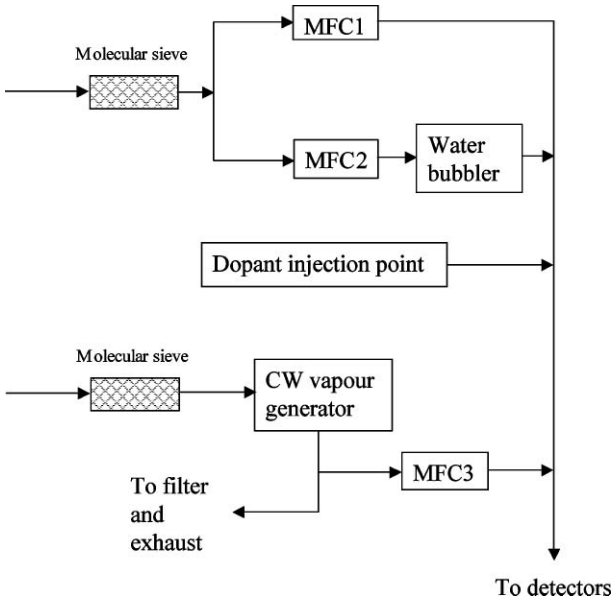

Fig. 2 Schematic representation of experimental set-up.

A constant vapour challenge of the CW nerve agent, tabun (GA) is delivered to the HiFAWS detection systems using a GI10 vapour generator (Graseby Ionics, now Smiths Detection, UK). The GA concentration in the bulk air stream has not been accurately quantified but is estimated to be 0.04 mg m^{-3}. For experiments using the Sionex SVAC instrument the total flow rate is maintained at 400 ml min^{-1} and a cell temperature of 35 °C. For experiments using the mass spectrometers, the total flow rate is maintained at 600 ml min^{-1} at a cell temperature of 35 °C.

3. Results and discussion

3.1. Dopants in IMS

The use of dopants in IMS to reduce the response from interfering chemicals has been successfully employed in military and security detection and monitoring equipment. The stated proton affinity (PA) of water is 165.2 kcal mol^{-1} [9] and in an undoped system the positive ion mode reactant ion is dominated by protonated water cluster ions of the form $H^+(H_2O)_n$. Any chemical with a higher proton affinity than that of water is likely to form a detectable product ion. Both acetone and ammonia are used as internal dopants for military IMS equipment. With proton affinities of 194.1 and 204.0 kcal mol^{-1} respectively,[9] use of these dopants results in a detection/monitoring system that is more selective for CW nerve agents (note the proton affinity of most organophosphates is greater than 210 kcal mol^{-1}) and less prone to undesirable responses from background chemicals.

The use of dopants in IMS will affect ion drift velocities (v_d). For example, the introduction of tabun (GA) to an undoped water-based IMS will result in the formation of the protonated monomer, $GA{\cdot}H^+{\cdot}(H_2O)_n$ whereas when introduced to an acetone-doped IMS, under otherwise identical conditions, a protonated, acetone-associated monomer, $GA{\cdot}H^+{\cdot}Ac{\cdot}(H_2O)_m$, is observed ($m < n$). Under the same drift tube conditions and at relatively low internal water concentration, the protonated monomer $GA{\cdot}H^+{\cdot}(H_2O)_n$ will have a lower average cross-sectional area and therefore a higher drift velocity and mobility than the acetone-associated GA monomer $GA{\cdot}H^+{\cdot}Ac{\cdot}(H_2O)_m$. In both cases, however, the monomer ion formed has a mobility value that is characteristic of the CW nerve agent and the use of dopant sources in IMS, generally, does not affect the ability to detect and identify the agent. Note that in both an undoped and an acetone-doped IMS system, a protonated GA dimer is also usually observed when GA is introduced at sufficiently high concentration.

3.2. Dopants in HiFAWS

The use of dopants in HiFAWS will produce similar product ions to those identified in IMS. However, in HiFAWS we are not concerned with differences in absolute mobility at low field (K_l) but in differences in mobility values at high and low field (K_h/K_l). In HiFAWS, unless there is a difference in the mobility of an ion as it oscillates between high and low field conditions the ion will pass through the cell and will not require a compensating voltage to correct for ion drift (CV = 0 V). If this behaviour continues as the peak electric field strength is increased, the ion will exhibit no field dependence. As will be highlighted, the use of traditional IMS dopants in HiFAWS can lead to CW agent product ions with little field dependence and a system with poor selectivity.

3.2.1. Water clustering/declustering in an undoped, water-based HiFAWS system. As recently described,[10] there are a number of mechanisms that may account for the difference between the high field and low field mobility of an ion. The role of a water clustering/declustering mechanism in HiFAWS is important[11] and work at Dstl has further highlighted the importance of this mechanism in influencing the field dependence of CW agent monomer ions.[12] A comparison of dispersion plots for GA at 10 ppm [Fig. 3(a)] and 1000 ppm [Fig. 3(b)] water concentration illustrates this effect. Whilst the GA dimer is largely unaffected by such changes in water concentration, the GA monomer is strongly affected, becoming more field dependent at increased water concentration.

HiFAWS/mass spectrometry gives an indication of the ions present under low field conditions as ions are transferred from the HiFAWS cell (at a user-selected CV), through an interface orifice and into the quadrupole mass spectrometer. When tuned to the CV required to detect the GA monomer at an applied peak rf amplitude of 1000 V (E = 20 000 V cm^{-1}), the mass spectra shown in Fig. 3(c) (10 ppm water) and Fig. 3(d) (1000 ppm water) were obtained. At a water concentration of 10 ppm, a protonated GA monomer, $GA{\cdot}H^+$ (m/z = 163) with some associated water clustering, $GA{\cdot}H^+{\cdot}(H_2O)_{1\text{–}3}$, is observed. At a water concentration of 1000 ppm there is a significant increase in low field water clustering around the GA monomer with the ions $GA{\cdot}H^+{\cdot}(H_2O)_{2\text{–}7}$ identified. This increase in low field water clustering as the water concentration is increased may account for the increased field dependence. The more water molecules associated with the protonated GA monomer under low field conditions, the greater the number of water molecules dissociated at high fields. The more water molecules dissociated from the protonated GA monomer ion at high fields, the greater

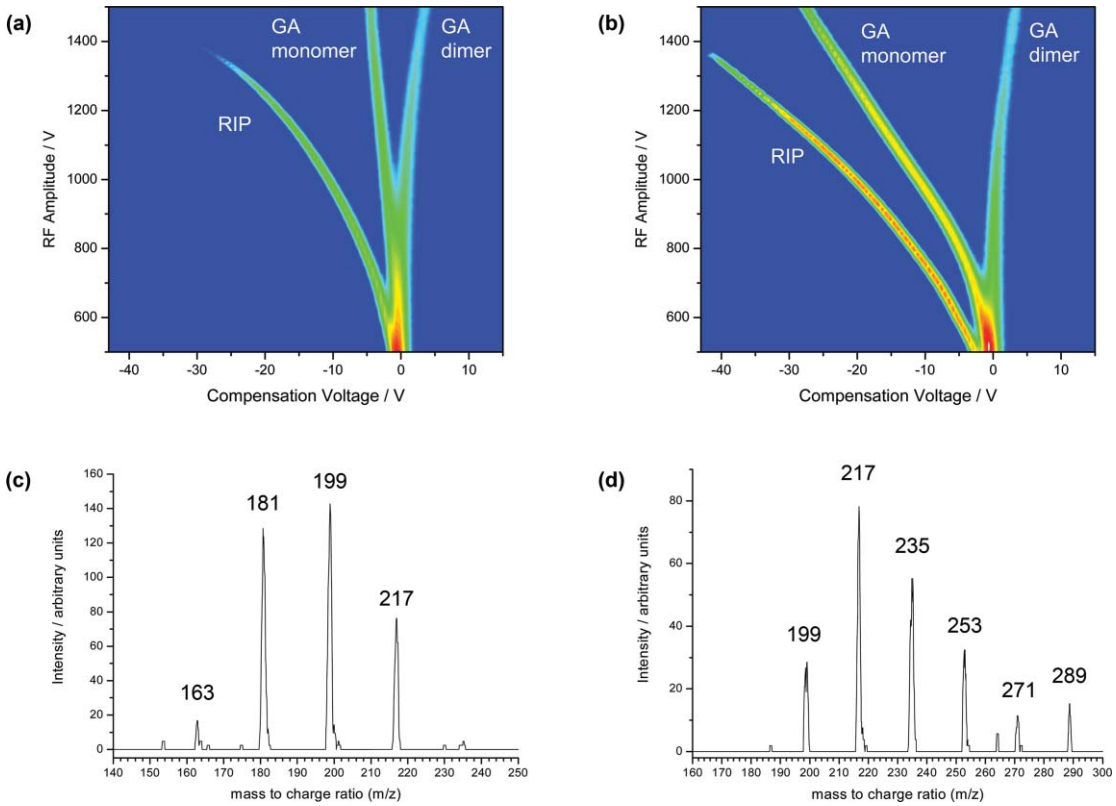

Fig. 3 (a) Dispersion plot of a GA challenge at 10 ppm water concentration; (b) dispersion plot of a GA challenge at 1000 ppm water concentration; (c) mass spectrum (rf amplitude = 1000 V) corresponding to GA monomer ions at 10 ppm water concentration; (d) mass spectrum (rf amplitude = 1000 V) corresponding to GA monomer ions at 1000 ppm water concentration.

the difference in high field and low field ion mobility value (*i.e.* K_h/K_l increases).

The field dependence of the GA dimer is observed to be largely independent of water concentration. Although not shown here, when the mass spectrometer was tuned to the CV required to detect the GA dimer ion, corresponding mass spectra indicate the presence of just the protonated GA dimer, GA·H$^+$·GA (m/z = 325) at 10 ppm and 1000 ppm water concentration. Indeed, the GA dimer ion behaves in a manner associated with an ion whose mobility value decreases when moving from low field conditions to high field conditions ($K_h/K_l < 1$). This behaviour has been reported in the literature previously[11] where the decrease in mobility at high fields was believed to be due to increased collisional size or increased strength of interaction between the ion and the carrier gas.

3.2.2. Effect of traditional IMS dopants in a HiFAWS system. The effect of adding traditional IMS dopants (ammonia and acetone) in a HiFAWS system is shown in the dispersion plots in Fig. 4. The response of the nerve agent GA (estimated challenge concentration 0.04 mg m^{-3}) in the presence of 200 ppm water is plotted when the HiFAWS system is undoped [Fig. 4(a)], ammonia-doped [Fig. 4(b)] and acetone-doped [Fig. 4(c)]. In each case, the dopant was delivered by headspace injection at a concentration of approximately 0.1 ppm. Clearly, the use of a dopant can have a dramatic effect on the appearance of the dispersion plots and the field dependence of the associated reactant and product ions.

3.2.3 Water clustering/declustering in a doped HiFAWS system. In the examples shown in Fig. 4, the GA monomer and dimer product ions become less well separated as the HiFAWS system is changed from undoped, water chemistry [Fig. 4(a)] to ammonia chemistry [Fig. 4(b)] and finally to acetone chemistry [Fig. 4(c)]. Whereas the field dependence of the GA dimer ions is largely unaffected by the addition of these traditional IMS dopant sources, the field dependence of the GA monomer ions is strongly affected. A water clustering/declustering mechanism can be used to account for this observed behaviour.

At 200 ppm water concentration in an undoped, water-based HiFAWS system [Fig. 4(a)], the mass spectrum obtained when tuned to the CV corresponding to the GA monomer ions (at an applied peak rf amplitude of 1000 V) contains peaks at m/z = 181, 199, 217 and 235 [Fig. 5(a)]. These peaks can be assigned to the ions GA·H$^+$·$(H_2O)_{1-4}$. This suggests that at a water concentration of 200 ppm there is sufficient low field water clustering around the protonated GA monomer to allow significant declustering at high fields and may explain the strong field dependence of the GA monomer.

The use of ammonia (0.1 ppm) as a dopant in a HiFAWS system at a 200 ppm water concentration [Fig. 4(b)] reduces the field dependency of the GA monomer ion. The mass spectrum obtained when tuned to the CV corresponding to the GA monomer ions (at an applied peak rf amplitude of 1000 V) contains peaks at m/z = 180, 198 and 216 [Fig. 5(b)]. These peaks can be assigned to the ions GA·NH_4^+·$(H_2O)_{0-2}$. Here, only two water molecules are associated at low field

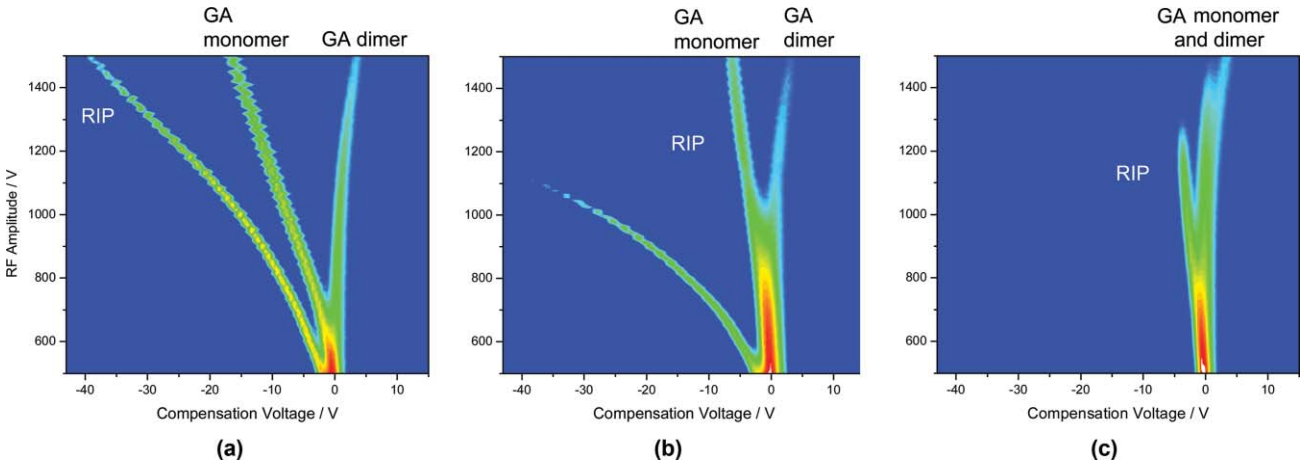

Fig. 4 (a) Dispersion plot (GA challenge, undoped) at 200 ppm water concentration; (b) dispersion plot [GA challenge, ammonia-doped (0.1 ppm)] at 200 ppm water concentration; (c) dispersion plot [GA challenge, acetone-doped (0.1 ppm)] at 200 ppm water concentration.

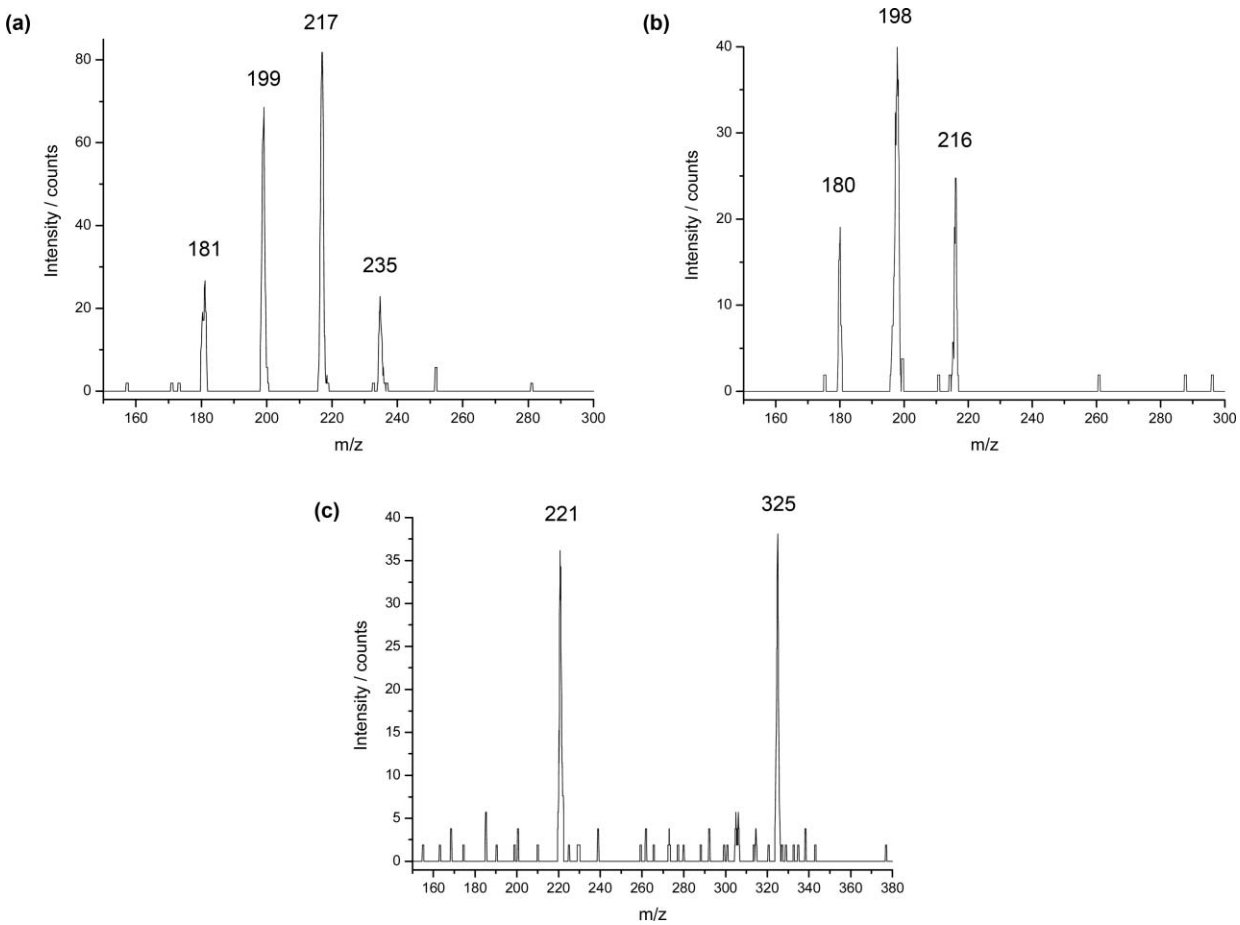

Fig. 5 (a) Mass spectrum (rf amplitude = 1000 V) corresponding to GA monomer ions at 200 ppm water concentration (undoped); (b) mass spectrum (rf amplitude = 1000 V) corresponding to GA monomer ions at 200 ppm water concentration [ammonia-doped (0.1 ppm)]; (c) mass spectrum (rf amplitude = 1000 V) corresponding to unresolved GA monomer and dimer ions at 200 ppm water concentration [acetone-doped (0.1 ppm)].

with the core $GA{\cdot}NH_4^+$ monomer ion. There is less water clustering/declustering occurring between the low and high fields when compared to the undoped HiFAWS system, which may account for the loss of field dependence of the GA monomer.

At 200 ppm water concentration in an acetone-doped (0.1 ppm) HiFAWS system, the GA monomer and dimer ions are not resolvable at an applied peak rf amplitude of 1000 V [Fig. 4(c)]. The mass spectrum obtained when tuned to the CV corresponding to these product ions is presented in Fig. 5(c). The

peak at $m/z = 221$ can be assigned to the acetone-associated protonated GA monomer ion ($GA{\cdot}H^+{\cdot}Ac$) and the peak at $m/z = 325$ to the protonated GA dimer ($GA{\cdot}H^+{\cdot}GA$). There is no evidence of additional peaks associated with water clustering. As these product ions do not readily cluster with water molecules there will be little difference in their respective high and low field mobilities. The GA monomer and dimer ions consequently exhibit similar field dependencies and are not well resolved. Acetone is evidently a very poor dopant for CW agent detection in conventional HiFAWS.

Conclusions

HiFAWS-based platforms have potential for improved CW agent detection and monitoring in military and security arenas. However, fundamental differences between IMS and HiFAWS means that dopant sources traditionally and successfully used in IMS may not be suitable for application to HiFAWS. The use of traditional IMS dopant sources in HiFAWS can result in product ions that exhibit little or no low field water clustering. Those product ions associated with sampled analytes are therefore likely to exhibit poor field dependence ($K_h/K_l \approx 1$) with similar spectral responses that cannot be distinguished.

The field dependence of CW agent monomer ions in HiFAWS is strongly influenced by a water clustering (low field)/declustering (high field) mechanism and work continues in this laboratory to find approaches to enhance this field dependence in order to improve selectivity.

Acknowledgements

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References

1 *Plasma Chromatography*, ed. T. W. Carr, Plenum Press, New York, 1984.
2 G. A. Eiceman and Z. Karpas, *Ion Mobility Spectrometry*, CRC Press, Boca Raton, 1993.
3 G. A. Eiceman and Z. Karpas, *Ion Mobility Spectrometry*, CRC Press, Boca Raton, 2nd edn, 2005.
4 E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases*, John Wiley & Sons Inc., New York, 1987.
5 I. A. Buryakov, E. V. Krylov, E. G. Nazarov and U. Kh. Rasulev, *Int. J. Mass Spectrom. Ion Processes*, 1993, **128**, 143.
6 I. A. Buryakov, A. L. Makas, E. V. Krylov, E. G. Nazarov, V. V. Pervukhin and U. Kh. Rasulev, *Sov. Tech. Phys. Lett.*, 1991, **17**(12), 60–65.
7 R Guevremont and R. W. Purves, *Rev. Sci. Instrum.*, 1999, **70**, 1370.
8 R. A. Miller, G. A. Eiceman, E. G. Nazarov and A. T. King, *Sens. Actuators, B*, 2000, **67**, 300.
9 NIST Proton Affinity Search compiled and evaluated E. P. Hunter and S. G. Lias.
10 E. G. Nazarov, S. L. Coy, E. V. Krylov, R. A. Miller and G. A. Eiceman, *Anal. Chem.*, 2006, **78**, 7697.
11 E. V. Krylov, E. G. Nazarov, R. A. Miller, B. Tadjikov and G. A. Eiceman, *J. Phys. Chem. A*, 2002, **106**, 5437.
12 S. K. Ross, presented at the 16th International Conference on Ion Mobility Spectrometry, held in Mikkeli, Finland, 22–27 July 2007.