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Letter

Reverse flow continuous corona discharge ionisation applied to ion mobility spectrometry

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Abstract

A prototype reverse flow continuous corona discharge (RFCCD) ionisation source has been designed and interfaced to an ion mobility spectrometer/mass spectrometer (IMS/MS). It has been demonstrated that when the air flow past the corona needle is reversed, ozone and NO_x can be removed from the reaction region. In the absence of ozone and NO_x, the concentration of unreactive ions such as CO_3^- and NO_3^- that are commonly observed when using continuous corona ionisation sources are significantly reduced. The results presented highlight the potential of RFCCD as a viable alternative non-radioactive ion source. (Int J Mass Spectrom 218 (2002) L1–L6)

Keywords: IMS; Mass spectrometry; Ozone; NO_x

1. Introduction

Ion mobility spectrometry (IMS) is one of the major technologies currently used for the detection and monitoring of chemical warfare agents, explosives and illicit drugs. It is also used for the monitoring of potential atmospheric pollutants. Air quality monitoring inside space shuttle cabins and submarines are two examples in which a knowledge of air quality is vital.

The majority of IMS devices use radioactive ionisation sources such as β emitting ^{63}Ni foil. The mechanism for the ionisation of air through collisions with high energy β particles is reasonably well understood [1,2]. The initial ionisation process ultimately leads to a stable concentration of both positive and negative reactant ions. Atmospheric pressure chemical ionisation (APCI) of the sample vapour with this reservoir of reactant ions results in the formation of characteristic product ions that can be observed at the IMS detector. The polarity of the ions detected is dependent on the direction of the electric field applied to the spectrometer reaction region and drift cell.

The output from radioactive ionisation sources is extremely stable. Furthermore, radioactive sources are small, relatively inexpensive and noise- and power-free, making them almost ideal ionisation sources. However, there is a significant administrative burden associated with the safety requirements of radioactive ionisation sources, such as the requirement for leak testing, disposal and transportation. The latter is

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particularly onerous when transporting large numbers of military detectors or monitors. There has therefore been considerable interest in producing non-radioactive sources with similar performance characteristics to those obtained using radioactive sources. Corona discharge ionisation [3,4], flame ionisation [5], UV-ionisation [6] and X-ray [7] sources have all been investigated, with corona discharge ionisation receiving the most attention in terms of research and development efforts. These efforts have resulted in the utilisation of pulsed corona discharge (PCD) ionisation sources in IMS devices [8]. However, attempts to find a suitable continuous corona ionisation source (which does not require voltage pulsing or synchronisation of the resulting ions with the entrance shutter pulse to the drift tube) have failed. Although the performance of continuous corona discharge ionisation sources can compare favourably with radioactive sources, under some conditions they do not, resulting in severe loss of sensitivity and/or more complex mobility spectra.

Work in this laboratory has demonstrated the potential of reverse flow continuous corona discharge (RFCCD) as a non-radioactive ionisation source for use in IMS devices. Preliminary results show that the performance characteristics of RFCCD compare favourably with radioactive sources in both positive and negative mode.

2. Experimental

The drift tube used for this work was a flexible, modular system designed and built in conjunction with Graseby Ionics (Watford, UK). It is constructed of alternating rings of gold-plated stainless steel and ceramic to define the fields and drift flows. The drift tube may be assembled with any convenient length of drift and reaction regions, in this instance 4 and 1.5 cm, respectively, with a field of about 200 V cm^{-1} in each region. The ion source is a self-contained unit as shown in Fig. 1. Neutrals formed close to the corona needle are removed from the source by the movement of the flushing gas flow, whereas ions are forced through the small hole into the reaction region by the

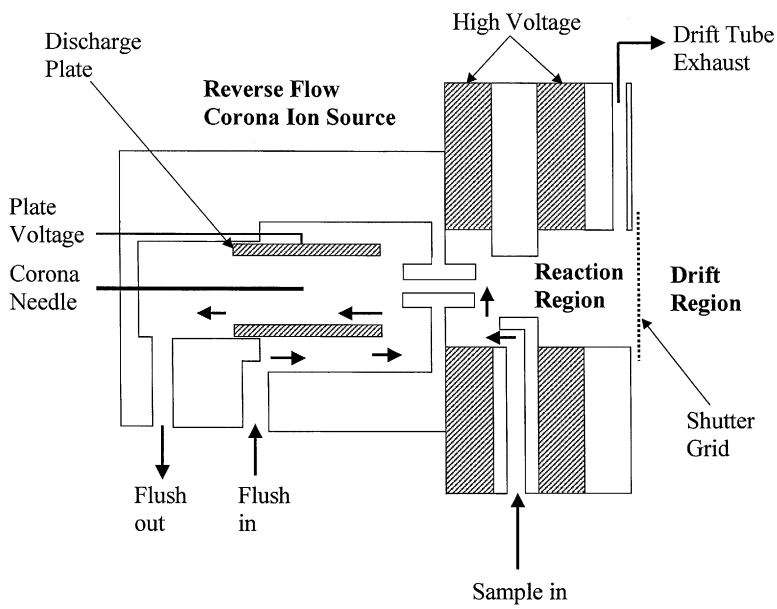

Fig. 1. Schematic diagram of prototype RFCCD ionisation source (The ‘flush in’ and ‘flush out’ are shown for reverse flow corona discharge ionisation).

imposed electric field. Ions produced by the corona source react with the sample admitted into the reaction region and are gated into the drift region using a Bradbury–Neilsen shutter. At the end of the drift region, ions are admitted into the mass spectrometer (VG Quadrupoles SXP Elite) via a 50 μm orifice in the ion collector. The drift and flush flows are dry air (10 ppm water) supplied by a pressure-swing drier (Pneudri, Domnick Hunter, Durham, UK). A photometric ozone (O_3) analyser together with a chemiluminescent NO_x detector (both Enviro Technical Services plc) were used to monitor O_3, NO and NO_2 concentrations.

3. Results and discussion

3.1. The effect of ozone and NO_x

The mechanism for the steady state production of reactant ions in continuous corona discharge ionisation is not well understood and is dependent on corona parameters such as shape, size and current. Other parameters (e.g. pressure, temperature and humidity) also influence the reaction chemistry. However, it is known that when using a continuous corona source neutral species such as ozone and oxides of nitrogen are produced [9]. It is suspected that these neutral species participate in reactions leading to reactant and/or product ions that differ from those observed when using a ^{63}Ni ionisation source.

Experiments were conducted to measure the concentration of O_3 and NO_x produced during positive and negative ion mode operation of a continuous corona discharge ionisation source. These experiments were carried out using three different stainless steel corona needles (10 and 50 μm diameter wires and a large APCI needle (10,000 μm tapering down to a point)) over a range of corona currents (0.2−20 μA). The air flow past the corona needle was 100 mL min^{-1} at all times.

It was found that the O_3 and NO_2 concentrations produced by corona discharge ionisation increased with increasing corona current in both positive and negative ion modes, whereas NO levels were low and relatively constant. In negative ion mode, the concentration of ozone produced at all corona currents was much higher (approximately by a factor of 10) than the total concentration of NO_x produced. In positive mode, very similar levels of NO_x were produced. Relatively high levels of O_3 were also detected, although not in such high concentrations as those observed when operating the corona source in negative ion mode. For example, in positive ion mode at a corona current of 1 μA, approximately 100 ppb O_3 was produced compared to approximately 500 ppb generated in negative ion mode. Increased levels of ozone in negative mode in a continuous corona discharge have been observed previously [10].

The concentrations of ozone and NO_x produced by a radioactive ^{63}Ni source (10 mCi, 370 MBq) were determined in a similar manner. The flow rate past the ionisation source was 100 mL min^{-1}. Only very low concentrations of O_3 and NO_x were detected in both positive and negative ion modes at levels close to the detection limit of the analysers (approximately 1 ppb). Earlier work [11] predicted that low concentrations of O_3 and NO_x would be generated in a typical radioactive ^{63}Ni ionisation source.

3.2. The effect of reverse flow continuous corona discharge ionisation

In order to determine the effect of O_3 and NO_x concentrations on reactant ion formation in an IMS system, a continuous corona discharge ionisation source was attached directly to a mass spectrometer. The work was focused on the behaviour of negative ions. The results obtained in negative ion mode when the rate of the flow past the corona needle was varied are shown in Fig. 2. Ion species such as O_3^-, CO_3^- and NO_3^- can be seen to dominate and the formation of O_2^- and $CO_2 \cdot O_2^-$ ions are completely suppressed. When the air flow in the ionisation source was directed in the opposite direction past the corona needle (see Fig. 1) the formation of O_2^- and $CO_2 \cdot O_2^-$ ions is favoured (Fig. 3). Reversing the direction of the air flow has a dramatic affect on the nature of the negative ion mode reactant ion peak when using a continuous corona source.

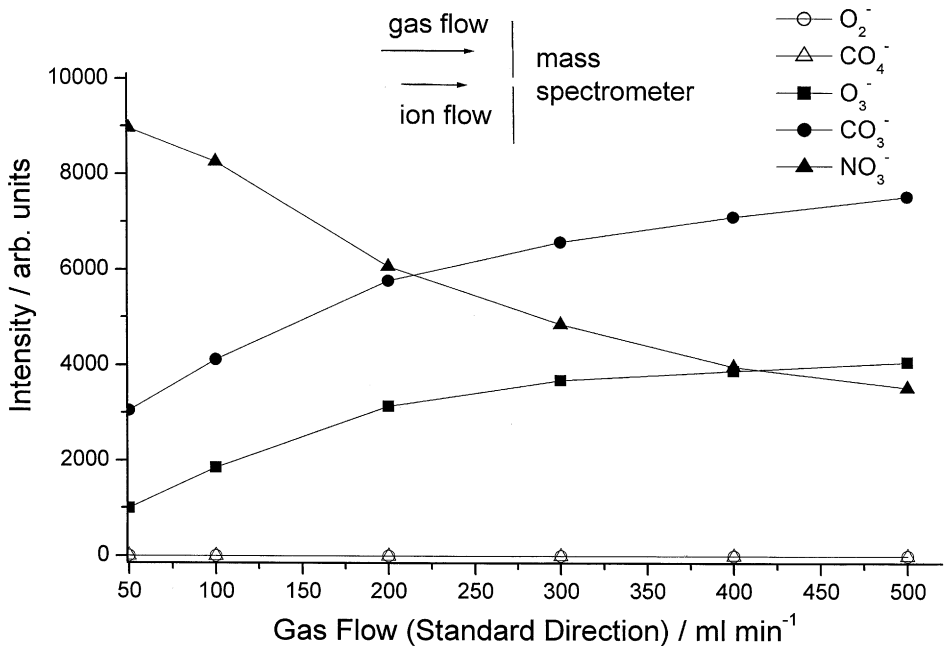

Fig. 2. Ions detected on mass spectrometer in negative ion mode (standard direction of air flow).

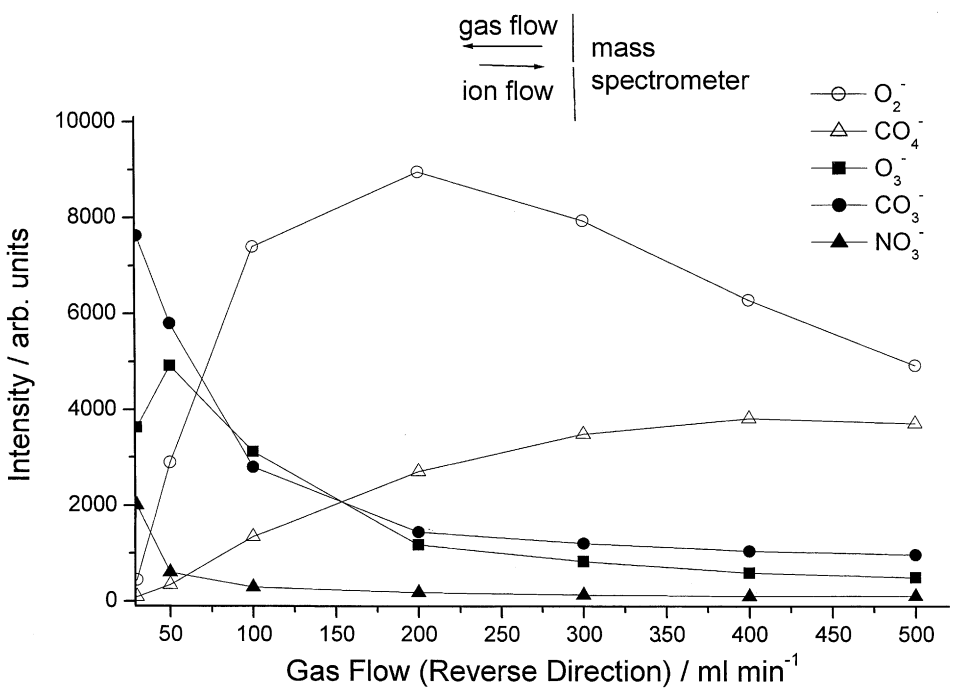

Fig. 3. Ions detected on mass spectrometer in negative ion mode when air flow is reversed.

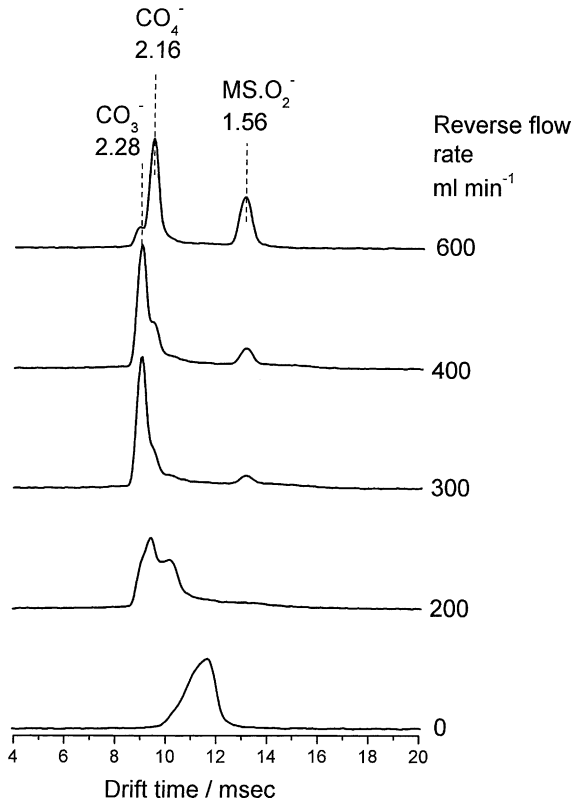

Fig. 4. IMS response to MS at different reverse flow rates (reduced mobility values in $cm^2\,V^{-1}\,s^{-1}$).

In IMS devices that use ^{63}Ni ionisation sources, methyl salicylate (MS) responds in negative ion mode producing the adduct product ion $MS{\cdot}O_2^-$ at a reduced mobility (K_0) of $1.56\,cm^2\,V^{-1}\,s^{-1}$. Experiments on a standard laboratory-based IMS system with a forward flow continuous corona ionisation source failed to produce a response to MS. However, as shown in Fig. 4, MS does give a response using a prototype reverse flow continuous corona ionisation source. These results were obtained despite using the large APCI corona needle set at a high corona current of 10 μÅ to purposely produce large quantities of ozone in the ionisation region.

There are two main observations. Firstly, the nature of the reactant ion peak (RIP) changes significantly as the flow past the corona needle is reduced. At high reverse flow (greater than 600 mL min^{-1}), the dominant peak at $K_0 = 2.16\,cm^2\,V^{-1}\,s^{-1}$ was mass identified as the O_2^- ion series that also includes the $CO_2{\cdot}O_2^-$ ion. The small peak at a slightly higher mobility of $K_0 = 2.28\,cm^2\,V^{-1}\,s^{-1}$, a shoulder to the dominant ion peak, was mass identified as being associated with the CO_3^- ion series. The RIP region at these high reverse flows is very similar to the negative-mode RIP obtained with a ^{63}Ni radioactive source in a standard IMS system. As the reverse flow past the needle is reduced, so the shape and position of the reactant ion peak changes. Initially, there is a shift of the RIP to the CO_3^- ion series at higher mobility values ($K_0 = 2.28\,cm^2\,V^{-1}\,s^{-1}$). This is observed at reverse flow rates between at 500 and 300 mL min^{-1}. As the reverse flow continues to decrease the RIP shifts towards lower mobility values, where ions associated with oxides of nitrogen (e.g. NO_3^-, NO_2^-, $NO_3^-{\cdot}HNO_3$) completely dominate the RIP. Secondly, at a high reverse flow (600 mL min^{-1}) the negative ion mode response of MS is similar to that obtained with a ^{63}Ni radioactive source with the single product ion peak, mass identified as the $MS{\cdot}O_2^-$ adduct, observed at $K_0 = 1.56\,cm^2\,V^{-1}\,s^{-1}$. As the reverse flow past the corona needle is lowered so the intensity of the $MS{\cdot}O_2^-$ product ion decreases. There is no evidence of the $MS{\cdot}O_2^-$ product ion at reverse flow rates of 200 mL min^{-1} or less.

Both these observations can be explained when the effects of ozone are considered. At high reverse flow rates ($\geq$600 mL min^{-1}) ozone produced by corona discharge ionisation is effectively flushed away from the ionisation region. This was confirmed by monitoring O_3 concentrations in both the flush outlet and drift tube exhausts (see Fig. 1). At a reverse flow of 600 mL min^{-1} the ozone concentration in the flush outlet exhaust was 3 ppm whilst in the drift tube exhaust it was 4 ppb. With ozone removed from the ionisation region, the dominant reactant ions formed are O_2^- and $CO_2{\cdot}O_2^-$ and these ions react with MS to form the $MS{\cdot}O_2^-$ adduct. As the reverse flow rate is reduced so the efficiency of ozone removal from the ionisation region decreases. For example, at a reverse flow rate of 10 mL min^{-1} the ozone concentration in the flush outlet exhaust was 0.3 ppm and in the drift

tube exhaust it was 1 ppm. At this reverse flow rate high concentrations of ozone are clearly being formed in the ionisation region and entering the reaction region. Reducing the reverse flow rate increases the deleterious effect of ozone, resulting in the formation of stable ions such as CO_3^- and NO_3^-, which do not react with MS.

Although the focus of this work has been on negative ion chemistry, in positive ion mode the formation of relatively high levels of ozone and NO_x in the corona discharge does not appear to significantly affect the reaction chemistry. It is worth noting, however, that work carried out in this laboratory using a continuous corona source in the positive ion mode has found evidence of ozonolysis reactions occurring with unsaturated and aromatic compounds. Use of RFCCD ionisation prevents these ozonolysis reactions from taking place.

4. Conclusions

The effect of reverse flow continuous corona discharge ionisation sources in IMS has been demonstrated. Ozone and NO_x generated by the corona discharge are effectively flushed from the ionisation region. This is of particular significance in negative mode operation where the formation of 'unreactive' ions such as CO_3^-, O_3^- and NO_3^- are inhibited and the usual reactant ions that are observed when using a radioactive ^{63}Ni source, such as O_2^- and $CO_2{\cdot}O_2^-$, dominate.

Work will continue in this laboratory to optimise the reverse flow continuous corona ionisation source with improvements to the source design assisted through the use of computational fluid dynamic (CFD) modelling.

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