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Positive corona discharge ion source with IMS/MS to detect impurities in high purity Nitrogen

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Abstract

We have applied the Ion Mobility Spectrometry/Mass spectrometry (IMS/MS) and the Atmospheric Pressure Chemical Ionisation/Mass spectrometry (APCI/MS) techniques to study the formation of the ions in the positive corona discharge (CD) in highly purified nitrogen with impurities at 100ppt level. The main products observed were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ions (reduced ion mobility of $2.15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Additionally, we have observed ions with reduced mobilities $2.42 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $2.30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The intensity of these ions was increasing with the increasing discharge current. We associated these peaks with NH_4^+ and $\text{NO}^+(\text{H}_2\text{O})_n$. The formation of these ions results from trace amounts of O_2 and NH_3 in nitrogen. The time evolution of the ions in corona discharge has been studied using the APCI/MS technique in the time windows ranging from $100\mu\text{s}$ to 2 ms. The present work indicates the ability of the IMS technique equipped with CD ions source to detect impurities below 100ppt level.

1. Introduction

Almost 50 years ago Shahin [1] performed first APCIMS studies of positive CD in atmospheric gases. He observed $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ as dominant ions. Decreasing the humidity and pressure of the gas he was able to observe primary ions formed in corona discharge [2]. The detailed description of the ions formed in positive CD in air under different discharge conditions (high and low values of CD currents) and mechanism of the NO^+ formation was given in previous studies [3,4].

Carroll et al. [5] studied the formation of positive ions in pure N_2 using radioactive ion source. Using the IMS/MS technique they detected $\text{NH}_4^+(\text{H}_2\text{O})_n$, $\text{NO}^+(\text{H}_2\text{O})_n$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. Kebarle et al. [6] studied formation of water cluster ions in IMS using mass spectrometric technique. They found out that one peak in IMS spectrum represents mixture of ions and their water clusters in thermodynamic equilibrium due to formation and dissociation of the cluster ions in the drift gas.

Tabrizchi and co-workers [7] investigated positive and negative CD as an ion source for IMS. The application of the corona discharge as ions source resulted in improved sensitivity of the IMS. One of the major problems in application of CD as ion source is the formation of large number of reactive molecular species in corona discharge which strongly influence the resulting spectra. Solution for this problem was suggested by Ross and Bell [8] who applied the reverse flow corona design. Different solution to this problem was the implementation of the curtain gas by Tabrizchi and Abedy. [9].

The NO^+ production as function of CD current and reverse flow rate in IMS in air was documented by Tabrizchi and Ilbeigi [10] in the attempt to optimize positive corona ion source for explosives detection. Ketkar and Dheandhanoo [11, 12] demonstrated IMS as a lower cost alternative to APCIMS technique [13] for monitoring the gas impurities in air at ppb level.

In this paper we present the IMS/MS and APCI/MS studies of the positive CD in high purity Nitrogen. We have measured the IMS spectra of the positive ions formed in CD as a function of discharge current and the particular ion peaks in the IMS spectra have been identified using the MS. The time evolution of the ions formed in the CD was studied using the APCDI/MS technique. Additionally, this work have demonstrated

the ability of IMS and IMS/MS systems equipped with CD to detect trace amounts of H₂O, O₂ and NH₃ in Nitrogen down to 100 ppt and 10 ppt levels.

2. Experiment

The IMS/MS (Figure 1a) and APCI/MS (Figure 1b) instruments equipped with point to plane corona discharge ion source were described in our previous work [14]. In attempt to reduce the penetration of the neutrals species and radicals formed in the corona discharge into the drift region we used single flow IMS system with gas outlet behind the corona discharge (reverse flow corona discharge). Two positive power supplies (Heinzinger) were used, one for corona discharge and one for the drift field. The electric field in IMS drift tube with total length 12.45 cm was 351,8 V/cm. In APCI/MS experiment the electric field in the short drift region was varied in the range 6000-250V/cm with corresponding drift time of ions from 0.1 to 2ms approximately. The current of the corona discharge was varied from 3 to 10 μ A (limited by HV power supply) in case of IMS/MS studies, while in the case of APCI/MS was at the constant value 10 μ A. The 5.0 nitrogen (Linde) was further purified (MICROTORR, MC190-903FV) in order to reduce the concentration of O₂, H₂O, CO, CO₂, H₂ impurities under 100ppt and NH₃ and amines under 10ppt. The drift tubes of IMS/MS and APCI/MS instruments were fed by nitrogen at flow rate 900mL/min. The drift tube has been operated at atmospheric pressure and room temperature (294 K).

The quadrupole mass spectrometer (Pfeiffer Vacuum QMH 420) has been located in the vacuum chamber and differential pumping has been applied in order to achieve high vacuum in the vacuum chamber with mass spectrometer. The transport of the ions from IMS into vacuum has been facilitated via 100 μ m orifice. First vacuum chamber has been pumped by rotary backing pump down to pressure of approximately 100 Pa, the second vacuum chamber has been pumped by pair of turbomolecular pumps with overall pumping speed of 500 L.s⁻¹ and the quadrupole mass spectrometer has been additionally pumped by 70 L.s⁻¹ turbomolecular pump.

The positive ions in the mass spectrometer have been detected by Secondary Electron Multiplier (SEM) using the single ion counting method. Using IMS/MS setup we were able to measure IMS spectra and mass resolved IMS spectra. With open shutter grid mass spectra of the ions passing through the IMS has been measured. The

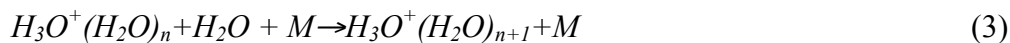
APCI/MS allowed us to measure mass spectra of the ions formed in the corona discharge at different time windows.

3. Results and discussion

3.1 IMS/MS study

Two peaks with drift times 12.6 ms and 13.4 ms were observed in IMS spectrum of positive corona discharge in pure N₂ at low discharge current of 3 μA (Figure 2a). The corresponding reduced ion mobilities of these peaks were 2.3±0.05 cm²V⁻¹s⁻¹ and 2.15±0.05 cm²V⁻¹s⁻¹. The intensity of the peak at 11.95 ms with corresponding reduced mobility 2.42±0.05 cm²V⁻¹s⁻¹ was close to limit of detection at corona current 3 μA. The increase of the corona current resulted in the increase of the peaks with reduced mobilities 2.42 cm²V⁻¹s⁻¹ and 2.3 cm²V⁻¹s⁻¹ and decrease of the peak with reduced mobility 2.15 cm²V⁻¹s⁻¹ as can be seen from Figure 2a. In the Figure 2b we show the mass spectrum measured at discharge current of 8 μA. The mass spectrum is dominated by H₃O⁺(H₂O)_n clusters, additionally at this high discharge current NH₄⁺ and NO⁺ ions are present in the spectrum.

We have measured mass resolved IMS spectra (Figure 3a), which revealed that the dominant peak with reduced mobility 2.15 cm²V⁻¹s⁻¹ is composed of the ions H₃O⁺(H₂O) (m/z=37) and H₃O⁺(H₂O)₂ (m/z=55). It was not possible to measure the position of H₃O⁺ (m/z=19) ions in IMS spectrum due to them relatively low intensity. We believe that the position of this ions in IMS spectrum will be the same like the position of the others H₃O⁺(H₂O)_n ions due to them drift in thermodynamic equilibrium. The H₃O⁺(H₂O)_n are formed from primary ions N₂⁺ through well know reactions [15]:



As the equilibrium constants for the reactions (3) are known, we are able to measure the water density from the intensity ratio of the H₃O⁺(H₂O)_n ions [6]. The ratio H₃O⁺(H₂O)₂/H₃O⁺(H₂O)=0.35 (Figure 2b) at temperature 295K gives water concentration of 94ppt. This result is in very good agreement with the values stated by the manufacturer of the purifier, which guarantee the removal of water from gas at <100ppt level.

The peak with the reduced ion mobility of $2.3\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is composed of the ions NO^+ ($m/z=30$) and $\text{NO}^+(\text{H}_2\text{O})$ ($m/z=48$). Position of the ion NO^+ in IMS spectrum is shown in the Figure 3a. Due to low intensity of the $\text{NO}^+(\text{H}_2\text{O})$ we were not able to detect it in mass resolved IMS spectrum. We assume that the formation and decay of $\text{NO}^+(\text{H}_2\text{O})_n$ ions is in thermodynamic equilibrium [6] and the cluster ion $\text{NO}^+(\text{H}_2\text{O})$ should be detected at the same position as NO^+ [5]. The presence of $\text{NO}^+(\text{H}_2\text{O})_n$ ions in positive IMS in “pure” nitrogen was in the case of radioactive ion source well documented by Karasek and Denney [16]. The mechanism of the NO^+ formation was proposed by Dunkin [17] and Hiraoka [18]:



where the ions NO_2^+ are not stable under IMS conditions [16]. The N_3^+ ($m/z=42$ figure 2b) was observed in MS only at high discharge currents. In the IMS we were not able to detect a peak which could be assigned to N_3^+ . However there also exist one pathway which should play important role in NO^+ formation [19]:



The sensitivity of IMS depends generally on the magnitude of the ion current generated in the ion source. In the case of IMS, the corona discharge ion source is much more intense than the radioactive source, which results in high detection limit for O_2 at 100 ppt level. The intensity of the NO^+ peak at high corona currents was relatively strong so the expected limit for O_2 detection could be one order of magnitude lower.

The first peak in the IMS with the reduced mobility of $2.42\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is composed of the ions with $m/z=18$ (Figure 3a). Since the H_2O^+ ions are not able to survive in IMS conditions [5] we assign this peak to the NH_4^+ ions. These ions are effectively formed via reaction [20]:



Despite the low concentration of ammonia (10ppt) in our nitrogen we are able to detect this ion in the IMS system. The ratios of the relative intensities of IMS peaks as a function of the corona current are presented in the Figure 3b.

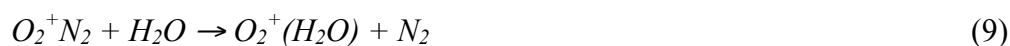
3.2 APCI/MS study

The APCI/MS technique was used to measure the time evolution of the ions formed in corona discharge. At high potential of the plate electrode we were able to detect ions in time scale of around 100 μs after the formation of the primary ions in discharge. At low potential the time window was around 1 ms. At short time the ions with $m/z = 19, 30, 32, 36, 37, 42, 46, 48, 50, 55, 60$ were detected (Figure 4a). The ions with $m/z= 19, 37$ and 55 are well recognized reagent ions under APCI conditions and belongs to group $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ [21]. The masses 30 and 48 can be associated to ions NO^+ and $\text{NO}^+(\text{H}_2\text{O})$ through reactions 5a and 6a. The ions with $m/z=32$ and 50 are formed through reaction 5b and 6b or via highly efficient charge exchange between N_2^+ and O_2 [19] and belongs to ions O_2^+ and $\text{O}_2^+(\text{H}_2\text{O})$. The fact that NO^+ and O_2^+ ions should be formed via reaction of N_3^+ with O_2 was confirmed by the appearance of both ions in APCI/MS spectrum. In the Figure 4b we see the relative intensities of the ions as functions of the plate electrode potential. This potential is related through the drift velocity to drift time of the ions. Even at high potential (6000 V) the kinetic energy of the ions is below the dissociation limit of the ions.

The ions with $m/z=42, 60$ and 46 we assign to N_3^+ , O_2^+N_2 and NO_2^+ (reaction 4 and 5c). The ions with $m/z=60$ can not be $\text{N}_3^+(\text{H}_2\text{O})$ because the reaction:



has relatively high reaction rate of $2.57 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ [22]. This ions was not observed in our mass spectrum due to them very fast reaction with water molecules [19]. The O_2^+N_2 ions undergo efficient reactions with water:



with high rate constant of $4 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ [23]. The N_3^+ ions formed in corona discharge are also precursors of the ions $\text{NO}^+(\text{H}_2\text{O})$ ions and intermediate ions $\text{O}_2^+(\text{H}_2\text{O})$ via reactions 5a and 5b.

We see in the Figure 4b that the intensities of the intermediate ions $\text{O}_2^+(\text{H}_2\text{O})_n$ were decreasing with the increasing drift time. On the other hand, the relative intensities of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ were increasing. It is due to effective conversion of the $\text{O}_2^+(\text{H}_2\text{O})_n$ ions into $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ [3]. The $\text{O}_2^+(\text{H}_2\text{O})_n$ ions are therefore not observed in IMS/MS due to long time scale (~ 10 ms). On the basis of the disappearance of the ions with $m/z=36$ with increasing drift time (Figure 4b) we assign these ions to $\text{H}_3\text{O}^+(\text{OH})$. These ions are formed through exothermic reaction [23]:



and react further with water [23]:



with high reaction rate of $1.4\times 10^{-9} \text{ cm}^3\text{s}^{-1}$. This explains the absence of these ions in IMS. Thus $H_3O^+(OH)$ and $O_2^+(H_2O)_n$ ions contribute to the growth of the relative intensity of the $H_3O^+(H_2O)_n$ with increasing drift time. The fact that ions NH_4^+ were not observed in this study suggests these ions are formed later in the drift.

4. Conclusions

We have presented IMS/MS and APCI/MS studies of positive corona discharge in high purity N_2 . These spectrometric techniques delivered more insight on the processes of the formation of stable positive ions in the positive corona discharge. The dominant positive ions formed in positive corona discharge and detected at the ms time scale were protonated water clusters $H_3O^+(H_2O)_n$ ($n=0..2$), however, with increasing discharge power NH_4^+ and NO^+ are formed more efficiently. The evolution of the ions in the corona discharge in the time windows between $100\mu\text{s}$ and 2 ms revealed important role of N_3^+ as precursor of stable $NO^+(H_2O)_n$ ions and the intermediate ions $O_2^+(H_2O)_n$. The $O_2^+(H_2O)_n$ further reacted with water molecules and formed stable $H_3O^+(H_2O)_n$ ions. Present work also demonstrated the ability of the IMS/MS technique to detect O_2 , H_2O and NH_3 impurities in N_2 at $<100\text{ppt}$ level.

5. Acknowledgment

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Figure captions.

Fig. 1. IMS/MS (a) and APCI/MS(b) instruments, 1-gas inlet, 2-gas outlet

Fig.2. Ion mobility (a) and related mass (b) spectrum observed by IMS/MS technique. The numbers in the IMS spectra indicate the values of the reduced ion mobilities in $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Fig. 3. Mass resolved IMS spectrum (a) and ratio of relative intensities of the peaks in dependence of corona current (b)

Fig. 4. Mass spectrum at high potential of the plate electrode (a) and the relative intensity of the ions as a function of the plate electrode potential (b)

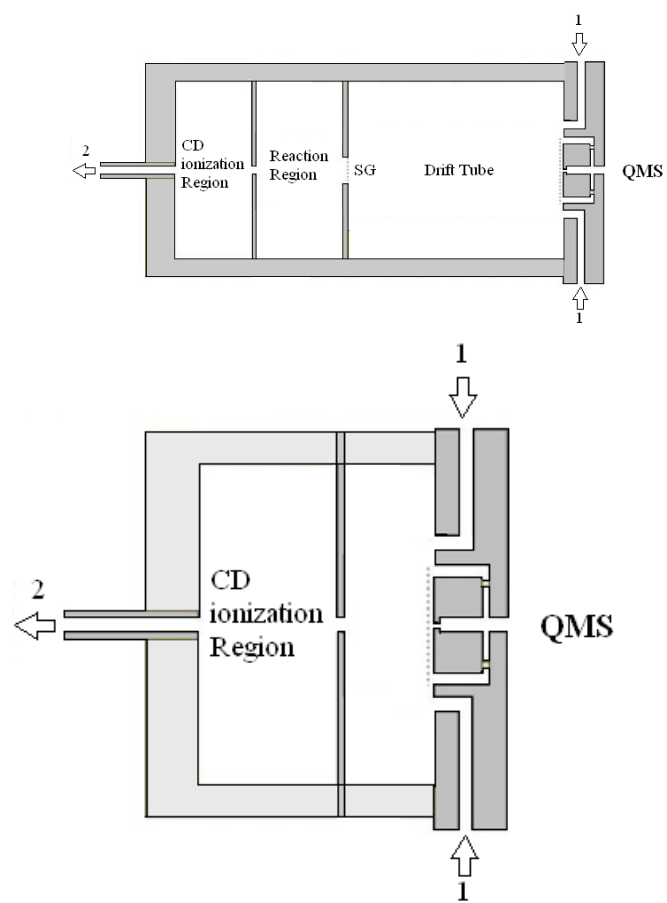


Fig. 1.

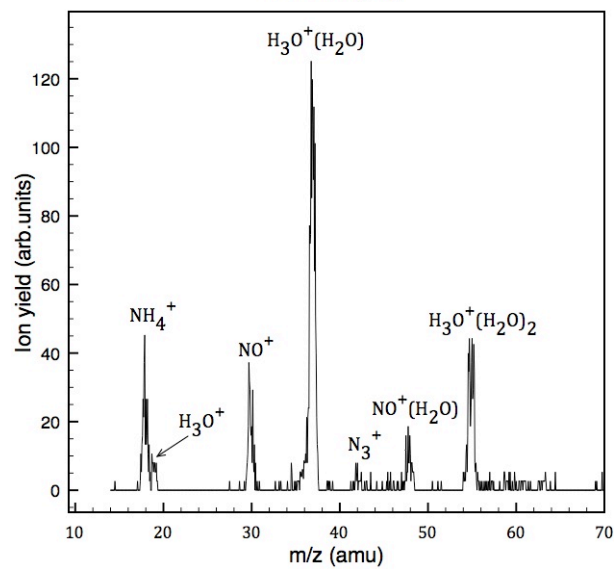
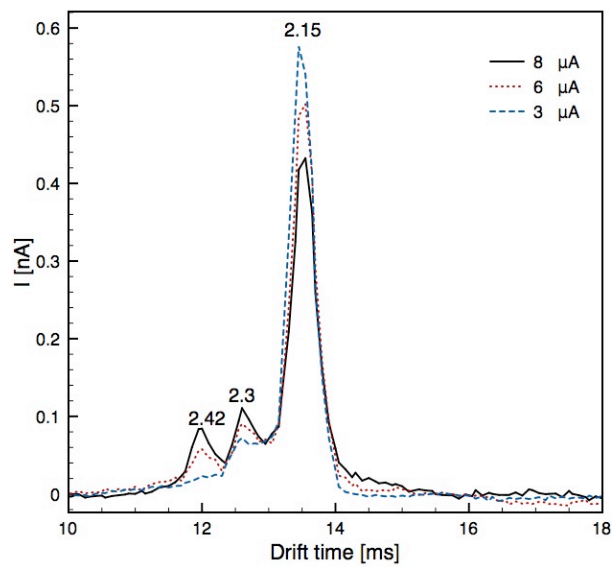


Fig.2.

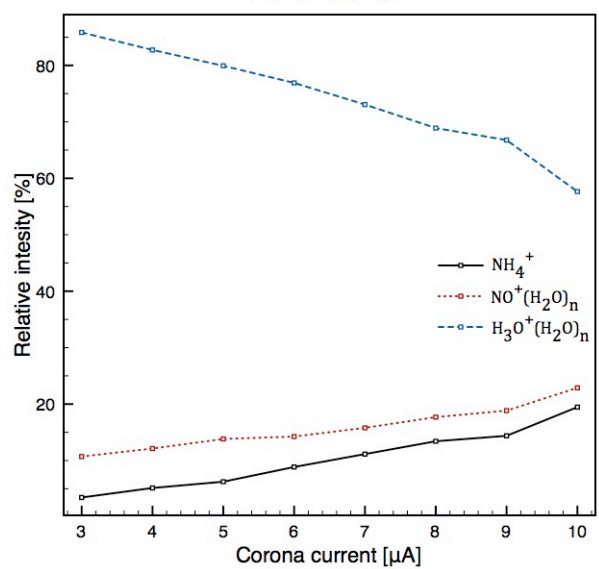
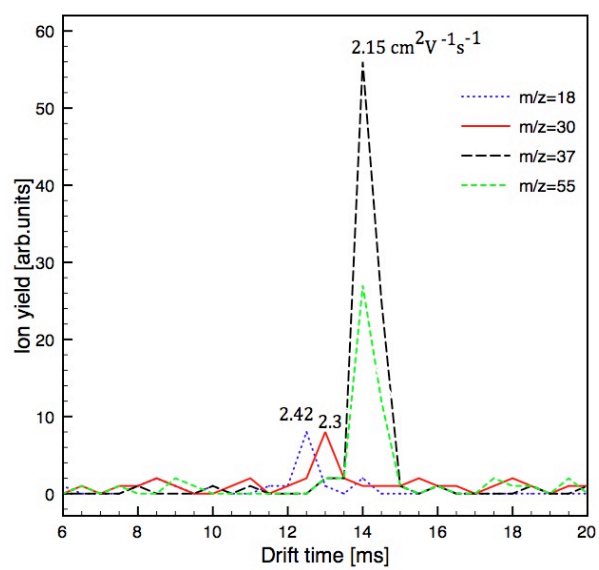


Fig. 3.

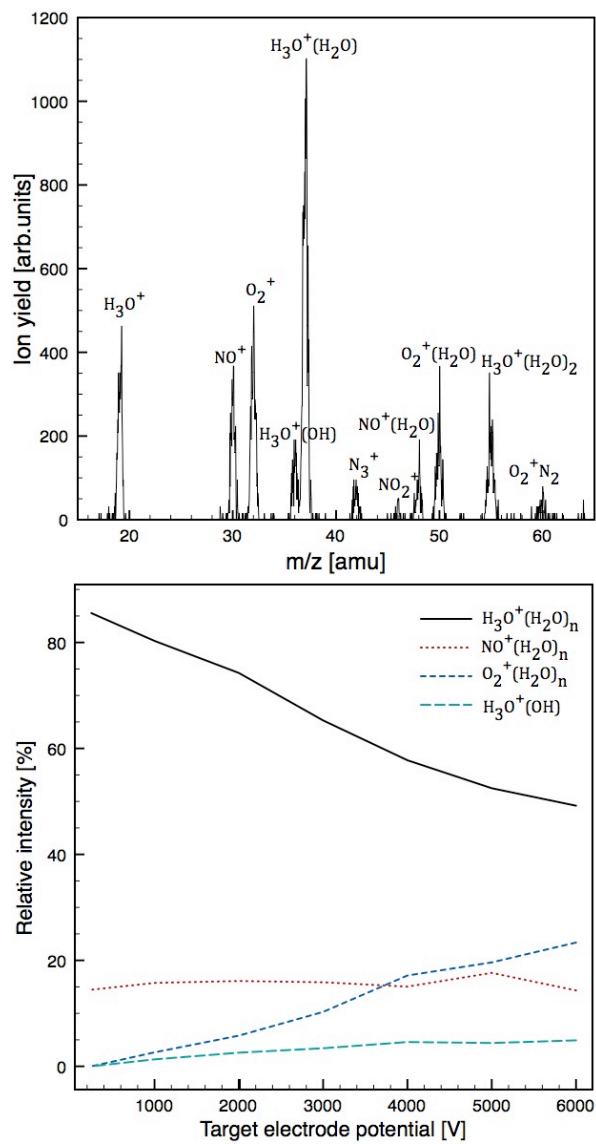


Fig. 4.