USING IMS EQUIPED WITH CORONA DISCHARGE TO DETECT TRACE AMOUNTS OF IMPURITIES IN HIGH PURITY NITROGEN

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We have applied the Ion Mobility Spectrometry/Mass spectrometry (IMS/MS) and the Atmospheric Pressure Corona Discharge Ionisation/Mass spectrometry (APCDI/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 H_3O^+(H_2O)_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 2.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}. These ions were increasing with the increasing discharge current. These peaks were associated with NH_4^+ and NO_2^-(H_2O)_n. These ions were formed due to presence of O_2 and NH_3 impurities in the nitrogen. On other hand this indicates the ability of the IMS technique and CD ions source to detect impurities below 100ppt level. Using the APCDI/MS technique we have monitored the time evolution of the ions in the CD.

1. Introduction

Almost 50 years ago Shahin [1] performed first Atmospheric Pressure Ionisation Mass spectrometry (APIMS) studies of positive corona discharge (CD) in atmospheric gases. He observed H_3O^+(H_2O)_n as dominant ions. Decreasing the humidity and pressure of the gas he was able to observe the primary ions [2]. Pavlík and Skalný [3] described in details the formation of the ions under different discharge conditions (high and low values of CD currents) and the formation of NO^+ in air. The ions NH_4^+(H_2O)_n, NO^+(H_2O)_n and H_3O^+(H_2O)_n were observed in the positive Ion Mobility Spectrum (IMS) in pure N_2 using radioactive ion source [4]. The ions and their water clusters were not resolved in IMS due to thermodynamic equilibrium between formation and dissociation of the cluster ions in the drift gas [5]. Tabrizchi and co-workers [6] optimized the CD as a ion source for IMS. The problem associated with strong production of new molecular species and radicals in CD were solved by Ross and Bell [7] who suggested the reverse flow corona design. Different solution to this problem was the implementation of the curtain gas by Tabrizchi et al. [8]. The NO^+ production as function of CD current and reverse flow rate in IMS in air was documented in [9] in the attempt to optimize positive corona ion source for explosives detection. Ketkar and Dheandhanoo [10, 11] demonstrated IMS as a lower cost alternative to APIMS technique [12] for monitoring the gas impurities at ppb level.

In this study we present the ability of IMS/MS and APCDI/MS systems to study positive CD. We demonstrate the ability of IMS and IMS/MS systems to detect trace amounts of H_2O, O_2 and NH_3 down to 100 ppt respectively 10ppt level in high purity nitrogen. Additionally, we have measured IMS spectra of the positive ions formed in CD as a function of discharge current and identified the ion peaks in the IMS spectra using the MS. The time evolution of the ions formed in the CD was studied using the APCDI/MS technique.

2. Experiment

The IMS/MS (Figure 1a) and APCDI/MS (Figure 1b) instruments equipped with point to plane CD ion source were described in our previous work [13]. In attempt to reduce the penetration of the neutrals and radicals formed in the CD into the drift region we used single flow IMS system with gas outlet behind the corona discharge. Two positive power supplies (Heinzinger) were used one for CD...
and one for the drift field. The drift field in IMS was 351.8 V/cm while in APCDI/MS was in range 6000-250V/cm with corresponding drift time of ions from 0.1 to 2ms approximately. The corona current in IMS was varied from 3 to 10μA (limited by HV power supply) while in APCDI/MS was at the constant value 10μA. The 5.0 nitrogen (Linde) was purified (MICROTORR, MC190-903FV) 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 APCDI/MS instruments were fed by high purity nitrogen with flow rate 900ml/min.

3. Results and discussion

IMS/MS study

Three peaks with drift times 11.95 ms, 12.6 ms and 13.4 ms were observed in IMS spectrum using positive CD in pure N₂ at low discharge current of 3μA (Figure 2a). The corresponding reduced ion mobilities of these peaks are 2.42±0.05 cm²V⁻¹s⁻¹, 2.3±0.05 cm²V⁻¹s⁻¹ and 2.15±0.05 cm²V⁻¹s⁻¹. The increase of the corona current resulted in 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 corona current 8μA. The mass spectrum is dominated by H₂O⁺(H₂O)ₙ clusters.

![Fig. 1. IMS/MS (a) and APCDI/MS (b) instruments](image)

![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 cm²V⁻¹s⁻¹.](image)
We have also measured mass resolved IMS spectra (Figure 3a), which revealed that the dominant peak with reduced mobility 2.15 cm$^2$V$^{-1}$s$^{-1}$ is composed of the ions H$_2$O$^+$ (m/z=19), H$_3$O$^+$(H$_2$O) (m/z=37) and H$_3$O$^+$ (H$_2$O)$_2$ (m/z=55). The H$_2$O$^+$ was not detected in this spectrum due to low intensity. The H$_2$O$^+$ (H$_2$O)$_n$ are formed from primary ions N$_2^+$ through well know reactions [14]:

$$N_2^+ + H_2O \rightarrow H_3O^+ + N_2$$
$$H_2O^+ + H_2O \rightarrow H_4O^+ + OH$$
$$H_3O^+ (H_2O)_n + H_2O + M \rightarrow H_3O^+ (H_2O)_{n+1} + M$$

As the equilibrium constants for the reactions (3) are known, we are able to measure the water density from the intensity ratio of the H$_2$O$^+$ (H$_2$O)$_n$ ions [5]. The ratio H$_2$O$^+$(H$_2$O)$_2$/H$_3$O$^+$(H$_2$O)=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 cm$^2$V$^{-1}$s$^{-1}$ is composed of the ions NO$^+$ (m/z=30) and NO$^+$(H$_2$O) (m/z=48). Position of the ion NO$^+$ in IMS spectrum is shown in the Figure 3a. Due to low intensity of the NO$^+$(H$_2$O) we were not able to detect it in mass resolved IMS spectrum. We assume that the formation and decay of NO$^+$(H$_2$O)$_n$ ions is in thermodynamic equilibrium [5] and the cluster ion NO$^+$(H$_2$O) should be detected at the same position as NO$^+$ [4]. The presence of NO$^+$(H$_2$O)$_n$ ions in positive IMS was in the case of radioactive ion source was well documented by Karasek and Denney [15]. The mechanism of the NO$^+$ formation was proposed by Dunkin [16]:

$$N_2^+ + N_2 \rightarrow N_3^+ + N$$
$$N_3^+ + O_2 \rightarrow NO^+ + O + N_2$$
$$\quad \rightarrow O_3^+ + N + O_2$$
$$\quad \rightarrow NO_2^+ + N_2$$

where the ions NO$_2^+$ are not stable under IMS conditions [15].

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$_3^+$. The sensitivity of IMS depends generally on the magnitude of the ion current generated in the ion source. In the case of IMS, the CD 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 drawback of the CD ion source is the generation of neutrals and radicals which may penetrate into the reaction region or drift tube and initiate there chemical reactions.

The first peak in the IMS with the reduced mobility of 2.42 cm$^2$V$^{-1}$s$^{-1}$ is composed of the ions with m/z=18 (Figure 3a). Since the H$_2$O$^+$ ions are not able to survive in IMS conditions [4] we assign this peak to the NH$_4^+$ ions. These ions are effectively formed via reaction [17]:

$$H_3O^+ (H_2O) + NH_3 \rightarrow NH_4^+ + 2H_2O$$

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.
APCDI/MS study

The APCDI/MS technique was used to measure the time evolution of the ions formed in CD. 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, 36, 37, 42, 46, 48, 50, 55, 60 were detected (Figure 4a). The ions with m/z = 19, 37 and 55 belongs to group H₂O'(H₂O)ₙ. The masses 30 and 48 can be associated to ions NO⁺ and NO⁺' (H₂O). The ions with m/z = 32 and 50 are formed through reaction 5b and belongs to ions O₂⁺ and O₂⁺' (H₂O). The fact that NO⁺ ions are formed via reaction of N₃⁺ with O₂ was confirmed by the appearance of both ions in APCDI/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.

We see in the Figure 4b that the intensities of the intermediate ions O₂⁺' (H₂O)ₙ were decreasing with the increasing drift time. On the other hand the relative intensities of H₂O'(H₂O)ₙ were increasing. It is due to effective conversion of the O₂⁺' (H₂O)ₙ ions into H₂O'(H₂O)ₙ [3]. The O₂⁺' (H₂O)ₙ ions are therefore not be observed in IMS 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 \((H_2O)_2^+\). These ions are formed through exothermic reaction [2]:

\[
O_2^+ (H_2O) + H_2O \rightarrow (H_2O)_2^+ + O_2
\]

(7)

The \((H_2O)_2^+\) ions are in next collision with water molecule converted into \(H_3O^+(H_2O)\) [2]. This explains the absence of these ions in IMS. \((H_2O)_2^+\) like the ions \(O_2^+(H_2O)_b\) contribute to the growth of the relative intensity of the \(H_2O^+(H_2O)_b\) with increasing drift time. The ions with m/z=42, 60 and 46 are \(N_3^+, N_3^+(H_2O)\) and \(NO_2^+\) (reaction 4 and 5c). Evolution of these ions due to their relatively low concentration is not depicted in the Figure 4b. The fact that ions \(NH_4^+\) were not observed in this study suggests these ions are formed later in the drift.

4. Conclusions

IMS are small portable and relatively inexpensive devices with fast response and low detection limits. Due to relatively low resolution of these instruments and also lack of data on the ion mobilities, the coupling of IMS with MS is of high importance, increases analytical capabilities of IMS and gives possibility to measure the mobilities of the ions. Moreover IMS/MS systems could deliver more insight on the ion-molecule reactions at atmospheric pressure. In this work we have presented the ability of IMS/MS system to study the CD and to detect \(O_2\), \(H_2O\) and \(NH_3\) impurities in \(N_2\) at <100ppt level.

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6. References