NO^+ generation and monoaromatic volatile organic compounds detection by IMS with positive corona discharge in wire to plate geometry

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The capability of corona discharge (CD) ionization source for monoaromatic volatile organics compounds (VOC) monitoring by IMS technique will be presented in this work. It is shown that sensitivity of monoaromatics VOC is better for NO^+ adduct ions. The generation of NO^+ reactant ions from CD for various CD current is also discussed in this work.

Introduction

Shahin [1] in his pioneering work on positive CD observed $H_3O^+(H_2O)_n$ as a dominant ions. The detailed formation of the positive ions ($H_3O^+(H_2O)_n$ and $NO^+(H_2O)_n$) in CD in air was well described in previous studies [3,4]. Carroll et all [5] investigated the formation of positive ions in ion mobility spectrometry (IMS) [6] and concluded that the main ions observed in IMS spectra are $NH_4^+(H_2O)_n$, $NO^+(H_2O)_n$ and $H_3O^+(H_2O)_n$. It was also shown that the different ions and their water clusters drift in thermodynamic equilibrium. The NO^+ as a reactant ions are important for monitoring monoaromatic VOC like benzene, toluene and m-xylene (BTX). Monitoring of such VOC is important for environmental and medical applications [7-10]. The formation of NO^+ in CD depends on many parameters like: discharge power, gas flow speed, flow directions and many others [3,11]. In this study we have investigated NO^+ formation in CD in wire to plane geometry as a function of CD current.

Experiment

The IMS instrument equipped with CD ionisation source in wire to plate geometry was interfaced to home made orthogonal Time-of-Flight mass analyzer (TOF). The IMS was operated in positive mode. In this experiment we have used oxygen and nitrogen gases of 5.0 purity (Linde) and we have the zero air prepared form mixture of these gases.

Results

The increasing CD current is responsible for higher neutral NO yield in CD gap [3]. The density of neutral NO is important for formation of NO^+ in CD [11]. The IMS spectra of zero air ionised using positive CD at discharge currents 10 and 50 μA is shown in Figure 1. It is evident from this figure that at elevated CD current we have achieved elevated NO^+ yield. The relative NO^+ yield from CD was at 10 μA is 18.5% while in the case of 50 μA discharge current it was 31%.

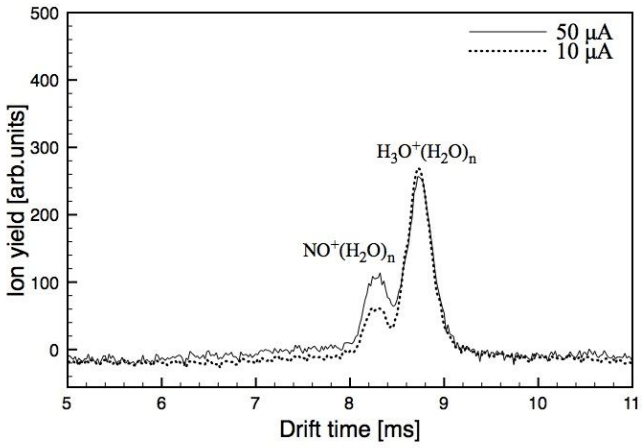

Fig. 1: IMS spectrum of $NO^+(H_2O)_n$ and $H_3O^+(H_2O)_n$ reactant ions for different CD current

The ions NO^+ and H_3O^+ drift in the IMS in thermal equilibrium with water vapors ($NO^+(H_2O)_{n-1}$ + H_2O + N_2 ⇄ $NO^+(H_2O)_n$ + N_2) as a result distribution of ions $H_3O^+(H_2O)_n$ and $NO^+(H_2O)_n$ is established which drift within one ion mobility peak.

The NO^+ ions are important precursor ions for chemical ionisation of the monoaromatic VOC via association reaction resulting in formation of $[M.NO^+]$ ions. The chemical ionisation via $H_3O^+(H_2O)_n$ results in formation of molecular ions $[M^+]$ (please note that $[M.H^+]$ formation via proton transfer reaction was not observed) [12]. However, the association reaction with NO^+ is more effective and results in higher sensitivity for detection of monoaromatic VOC. The two dimensional map of BTX molecular and NO^+ adducts ions measured in zero air is depicted in the Figure 2. The sensitivity of IMS for NO^+ adduct ions of BTX compounds was 1.5, 1.4 and 2.6 ppb respectively, while in the case of ionisation via $H_3O^+(H_2O)_n$ and formation of $[M^+]$ the sensitivity was up to 20 times lower (37, 41 and 72ppb).

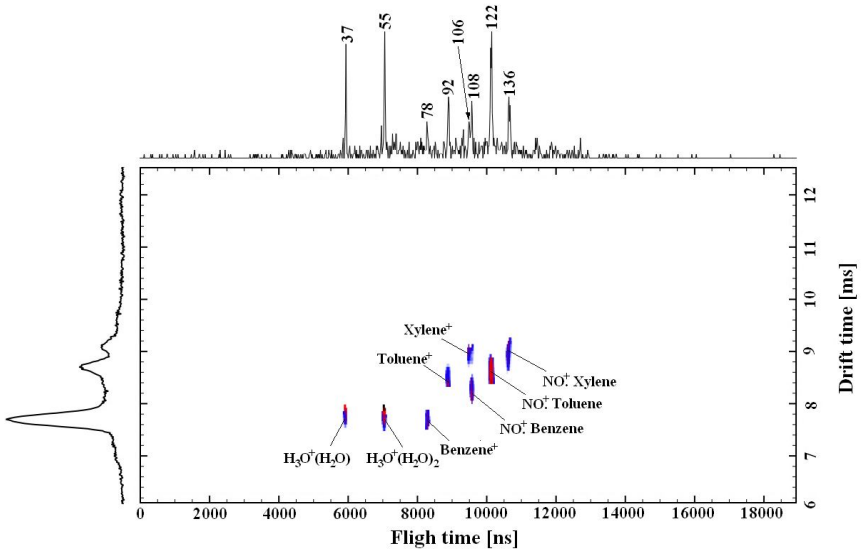

Fig. 2: 2D IMS/MS map of BTX molecular and NO^+ adducts ions measured in zero air.

Conclusions

The positive CD in air has been tested as ion source for APCI in IMS/MS with of $H_3O^+(H_2O)_n$ and $NO^+(H_2O)_n$ ions for monitoring of VOC (BTX). The dependence of the formation of NO^+ on the CD current was observed and higher sensitivity for BTX detection was achieved in the case of NO^+ ions.

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