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A Planar Gas Sensor Based on Mobility Spectrometry for Chemicals On-line Detection

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With concern for chemical attacks from terrorism, there is an urgent need for a method which can continuously and accurately detect hazardous chemicals. In this study, a planar gas sensor based on mobility spectrometry was demonstrated, which can get spectra for chemical detection in one second. Corona discharge (CD) is used as the ionization source. Three kinds of hazardous chemicals are measured and spectra exhibits remarkably differences. This planar gas sensor based on mobility spectrometry is a promising method for trace hazardous chemicals detection.

Keywords: Gas sensor, Hazardous chemical, Corona discharge.

INTRODUCTION

Hazardous chemicals include nerve agents, blister agents, asphyxiants and pulmonary irritants[1-2], which are harmful to human being and also destroy the environment. Enormous efforts have been made *via* spectrophotometry, non-dispersive infrared spectroscopy, mass spectroscopy (MS), high performance liquid chromatography (HPLC), ion mobility spectroscopy (IMS) and high-field asymmetric waveform ion mobility spectrometry (FAIMS). Among various methods, high-field asymmetric waveform ion mobility spectrometry as a new gas-phase analytical method has attracted much attention due to facile operation at ambient pressure, simplicity instrumentation, comparatively low costs and high sensitivity.

High-field asymmetric waveform ion mobility spectrometry utilizes significantly higher electric fields and identifies the ion species based on the difference in its mobility coefficient in high and low strength electric fields[3]. This is based on an observation of Mason and McDaniel[4] who reported that the mobility of an ion is affected by the applied electric field strength. Above an electric field to gas density ratio (E/N) of 40 Td (E > 10,700 V/cm at atmospheric pressure) the mobility coefficient K(E) has a non-linear dependence on the field. This dependence is believed to be specific for each ion species.

In the present work, a gas sensor based on FAIMS with corona discharge ionization source is fabricated and the capability on detecting chemicals is investigated. Three kinds of chemicals are tested. Specifically, separation voltages effect on ion mobility is observed and alpha function, which describes mobility's a non-linear dependence on the field, is calculated.

EXPERIMENTAL

The gas sensor was constructed. The schematic sketch of the sensor is shown in Fig. 1, which mainly consists of two planar ion filter electrodes (1), a deflector electrode (2) and a detector electrode (3). The detail parameters of FAIMS are given in Table-1. A hole in the upper wafers provides a means for introducing the reaction ions. After ionization of the gas sample, the ions are carried by a carrier gas flow through the ion filter region. Once through the ion filter, the ions are deflected onto a detector electrode. Depending on the polarity of the deflect electrode either negative or positive ions are measured at the detector electrode. Corona discharge ionization source consists of a sharp tungsten needle, a target electrode of metal mesh and a DC high voltage (HV) power supply (30kV, 1mA), which is a kind of point-to-plain geometry.

The gas sensor is operated using specialized electronics containing a separation waveform (U_d) generator, a compen-

TABLE-1
MAIN PARAMETERS OF THE GAS SENSOR

Component	Parameter
Filter electrode (1) (mm × mm)	11 × 5
Deflector electrode (2) (mm × mm)	5 × 5
Detector electrode (3) (mm × mm)	5 × 5
Distance between 2 and 3 (mm)	0.3
Carrier gas	Nitrogen
Carrier gas flow (l/min)	2
Temperature (°C)	25
Pressure (kPa)	101
U_{DC}	+12V

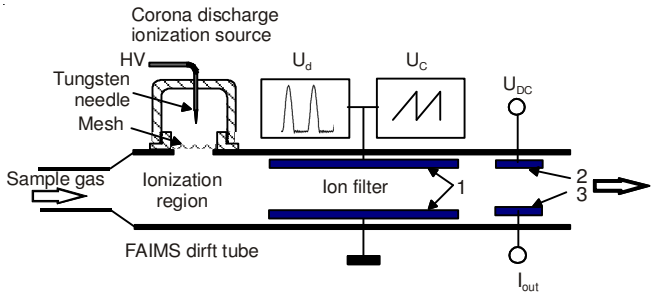

Fig. 1. Schematic of gas sensors

sation voltage (U_c) generator and a weak signal (I_{out}) amplifier. The seperation waveform generator could output variable peak-to-peak amplitudes of the asymmetric waveform range from 0 to 1500 V and the operating frequency of the generator is 1 MHz. The U_c is scanned between +21V to -21V in 1s periods.

Clean nitrogen was provided by Praxair Inc. with gas scrubbing through 13X molecular sieve. Purified nitrogen split into three independently controlled parts with a flow of 0-2 L/min used as the carrier gas flow (MFC1), 10-100 mL/min used to control samples (MFC2), and 0-300 mL/min used as waste flow (MFC3). Sample vapors were prepared using Teflon permeation tubes which were located in a thermo-stated container at 35-70 °C *via* a PID controller. This flow system allowed a constant flow to be delivered to the drift tube while permitting changes in vapor concentration by adjusting the ratio of sample to dilute flows. The diffusion of permeation tubes was weighed over several days to gravimetrically determine consumption of the sample (dm/dt). Which could estimate the concentration of sample in the gas flow.

Three kinds of chemicals used in this work without further purification. Diethylaminoethanol (DEEA, CAS 100-37-8) was purchased from Aldrich Inc. 2-Chloroethyl ethyl sulfide (2-CEES, CAS 693-07-2) was from Aladdin Inc. Dimethyl methylphosphonate (DMMP, CAS 756-79-6) was from Alfa Inc.

RESULTS AND DISCUSSION

Gas sensor spectra for chemicals: Gas sensor spectra for background and three kinds of chemicals in at separation voltage (U_d) of 800 V are shown in Fig. 2. All spectra exhibited 2-3 peaks for compensation voltages range from -10 to +5 V. The absence of peaks between compensation voltages of -10 to -20 V suggested that little fragmentation of the product ions had been observed. Ion peaks of chemicals in gas sensor spectra suggest that the product ion intensity was concentration dependent, but compensation voltage (U_c) was independent of concentration.

The product ions in positive polarity corona discharge contain N_2^+, N_4^+, $NH^+(H_2O)_n$ and $H^+(H_2O)_n$ (n is correlated with moisture). $H^+(H_2O)_n$ is commonly dominant ion and called the reactant ions, which can be observed at U_d from 400 V to 700 V.

Top spectrum shown in Fig. 2 is a background spectrum without chemicals vapors. The low intensities for the ion peaks were at a compensation voltage of -1V to -3V (peaks 1 and 2). Peaks 1 and 2 may be some impurities coming from corona discharge. The spectrum for dimethyl methylphosphonate showed

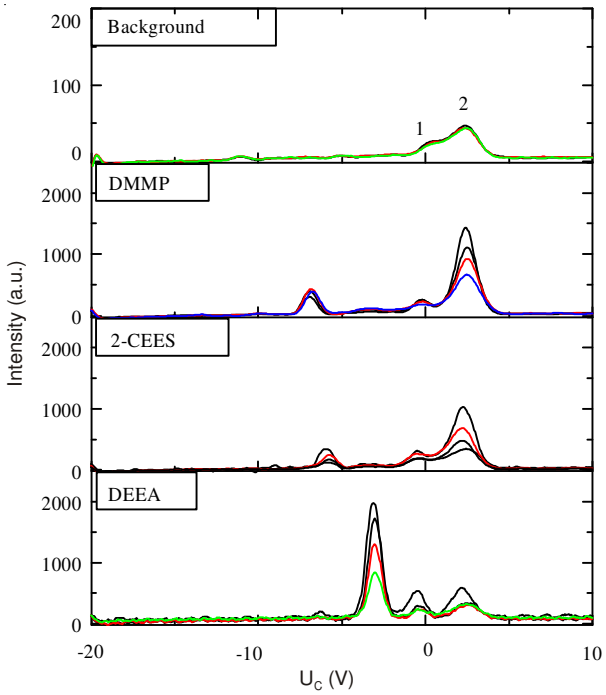

Fig. 2. Spectra of three chemicals under concentration of 80, 70, 60, 50 ng/L[3]

peaks at compensation voltage of -6.9V, -0.5V and 2.5V. According to existing result[5], peaks at -6.9V, 2.5V are protonated monomer and proton-bound dimer of dimethyl methylphosphonate. Similar results were obtained in the spectra of 2-CEES and DEEA The right peaks and left peaks were thought to be protonated monomers and proton-bound dimers, respectively. Chemicals have higher proton affinity than most chemicals 6, which could minimize the impact of impurities.

Separation voltage effect: The separation voltages (U_d) have influence on ion mobility and compensation voltages (U_c) for ion peaks are changed with ion mobility. Table-2 is given for U_d *vs.* U_c of CWA simulants. Increased electric field strength in the asymmetric waveform, resulted in increasing negative voltage to restore the transport of ions through the drift tube. This polarity is consistent with ions that exhibit increased mobilities with increased field strengths.

TABLE-2
U_d *vs.* U_c FOR THREE CHEMICALS

U_d(V)	U_c (V)		
	Dimethyl methylphosphonate	2-Chloroethyl-ethyl sulfide	Diethylamino-ethanol
450	-1.20	-0.23	-0.30
500	-2.55	-1.03	-0.71
550	-2.90	-1.35	-0.98
600	-3.20	-1.97	-1.38
650	-4.34	-2.59	-1.77
700	-5.50	-3.18	-1.97
750	-6.40	-3.74	-2.26
800	-6.90	-4.20	-2.54

Limits of detection: In order to investigate the sensitivity of gas sensor for chemicals, a permeation tube of dimethyl methylphosphonate calibrated by VICI corp. (70 °C 25 ng/min) was used to produce trace dimethyl methylphosphonate vapor

ranged from 1 to 12.5 ng/L^3. Response curve for dimethyl methylphosphonate is shown in Fig. 3. From 1 to 12.5 ng/L^3, the response of gas sensor has the linear relation the concentration of dimethyl methylphosphonate and the limit of detection (LOD) is below 1 ng/L^3.

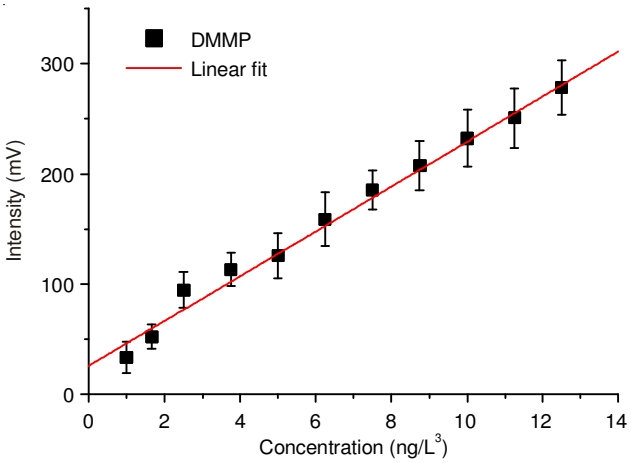

Fig. 3. Intensity *vs.* concentration for dimethyl methylphosphonate

Conclusion

Three chemicals are tested by a gas sensor based on mobility spectrometry and spectra exhibits remarkably differences. Ion mobility of chemicals increase with separation voltage ranged from 450 to 800 V. Dimethyl methyl-phosphonate is used as an example to investigate the capability of detecting chemicals and the limited of detection is below 1 μg/m^3 by gas sensor, which is a promising method for trace chemicals detection.

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