Improved Ion Mobility Spectrometer for Chemical Warfare Agents Detection

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Abstract: On the basis of existing Ion Mobility Spectrometry (IMS) technology, significant improvements have been made in drift tube design, gas path system structure, ionization source choice, and display screen. Then, a series of experiments on Sarin (GB), Mustard gas(HD), Hydrogen cyanide (AC) and VX detection have been launched, whose results indicated that the improved Ion Mobility Spectrometer had good performance in fast response speed, easy rinse, low temperature environment adaption with a high resolution and sensitivity.

1. Introduction

Having good performance in wide detection range, fast response, high sensitivity and database renewability, Ion Mobility Spectrometer has been widely used for quality checkout [1], toxic gas monitoring [2, 3], chemical warfare agents' detection [4-6], drug and explosive goods inspection [7-10]. It has become an important tool for airport and train station staff, security personnel and narcotics squad. But for some intrinsic technology reasons, IMS instrument has always been perplexed in false alarm or missing alert, troubled in humidity interference. So it is difficult to distinguish ions which have very similar mobility times with a low resolution IMS tool. The problems above have to be solved urgently.

In addition, IMS encounters many problems such as no response, system halting, blurred screen and so on in extreme environment. The phenomenon has been troubling users for a long time. As to application in Chemical Warfare Agents (CWAs) detection in war circumstance, the environment would be more severe. Therefore, it is the time to develop an improved ion mobility spectrometry to meet the needs and it is of great significance.

2. Experiment

2.1 The ionization source choice

Ion sources types include radioactive ionization, ultra violet lamp ionization, corona discharge ionization, atmospheric pressure glow discharge (APGD) ionization, dielectric barrier discharge (DBD) ionization and pulse discharge ionization et al. Ionization efficiency differs from different ionization source type, radioactive ionization source is under severe control by government and APGD ionization source has trouble in miniaturization. In order to get higher ionization efficiency and detection sensitivity, this paper has developed and selected impulse discharge as final ionization source on the former research basis of ^{63}Ni radioactive ionization source.

2.2 Ion mobility tube design

The design diagram for ion mobility tube is shown in Figure1.As an important separate place for ions, ion mobility tube performance directly decides mobility efficiency and final resolution. Material, effective mobility channel size, deflecting electric field strength, connection status to ionization source and signal collection electrode affects the mobility tube performance.
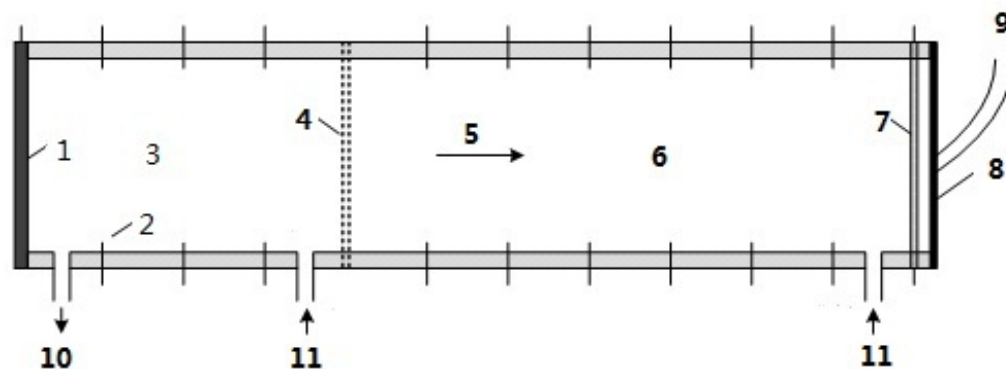
1. radioactive source; 2. electrode; 3. ionization area; 4.ion gate; 5. ion mobility direction; 6. ion mobility area; 7. grid; 8. ion receiver plate; 9. signal pins; 10. gas outlet; 11. gas inlet.

Figure 1. Ion mobility tube structural diagram

2.3 Ion mobility ratio and mobility time establishment

$$V_d = K \times E \tag{1}$$

$$K = \frac{3Ze}{16N_0} \times \sqrt{\frac{2\pi}{\mu kT}} \times \frac{(1+\alpha)}{\Omega_D} \tag{2}$$

$$K_0 = K \times \frac{133.32P}{760} \times \frac{273.16}{T} \tag{3}$$

Generally, mobility ratio K is a key parameter to indicate ion mobility speed, which is related to electric field strength (equation 1), charge number of ion, reduced mass of ion, density of mobility gas molecule and average collision area between ion and molecule (equation 2). Usually, reduced mobility ratio K_0 is used to express K in standard temperature and pressure condition (equation 3). As soon as the equation for K_0 and T (mobility tube temperature) was established, we could get the certain K_0 at a certain temperature (T). Then ion mobility time (t) is determinate by K_0, so different samples are easy to distinguish by difference in t. Accuracy grade in t determines the resolution of IMS instrument.

2.4 Gas path system structure

IMS instrument has always been suffered with the problem that signal has trouble in returning to baseline level quickly for high concentration samples especial for difficult volatile ones. This affects normal use because of a long time rinse. This paper has a delicate design in gas path structure. Waterproof and breathable material membrane has been placed in ion mobility tube inlet gas pipeline. So ethanol or other solvent could be directly injected into the gas inlet to rinse the gas path avoid contaminating ion mobility tube. Baseline restoration is attained soon.

2.5 Display screen material selection

The common display screen chooses LCD (Liquid crystal display) or LED (Light-Emitting Diode) screen cannot work in cold condition because of the liquid crystal molecule interior characteristic or outside induced screen malfunctions. The paper selects OLED (Organic Light Emitting Display) for the IMS instrument. Compared to LCD or LED, OLED has many advantages such as self-lighting, wide viewing angle and extreme high response speed. It's thinner, flexible with stronger temperature adaptation.

On the basis of the investigation and preparation above, IMS instrument has been assembled finally (Figure 2) and it has been extensively tested and debugged.
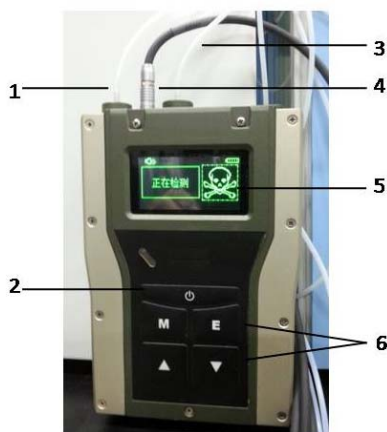
1. gas inlet pipeline; 2. power switch; 3. gas outlet pipeline;
4. power supply and data line; 5. display screen; 6. control buttons

Figure 2. Physical graph of IMS equipment

2.6 Sample gas generator and quantitative analysis

Placed liquid CWA in diffusion tube, which was put in the U-shape glass tube, toxic vapor diffuses outside the diffusion tube wall and mixes with dilution air gas. We can get a steady concentration CWA dynamic flow by this way. The concentration is very convenient to adjust by adding or reducing diffusion tubes, changing the dilution gas flow volume, altering cold trap or bath temperature. Analysis methods are mainly by chemical colorimetric determination and subordinately by GC-MS.

2.7 IMS instrument database establishment and test

Having been placed in incubator, IMS instrument was connected to the power line, inlet and outlet pipeline. Air flow was first passed through, then turned to CWA flow when the resistance baseline becomes steady. Data is recorded automatically by software on computer. On the database establishment stage, temperature program was increased from -25℃ to 45℃ at 0.01℃/S speed. HD, GB, HCN and VX were tested one by one. High and low concentration for 4 CWAs above was test at 25℃.

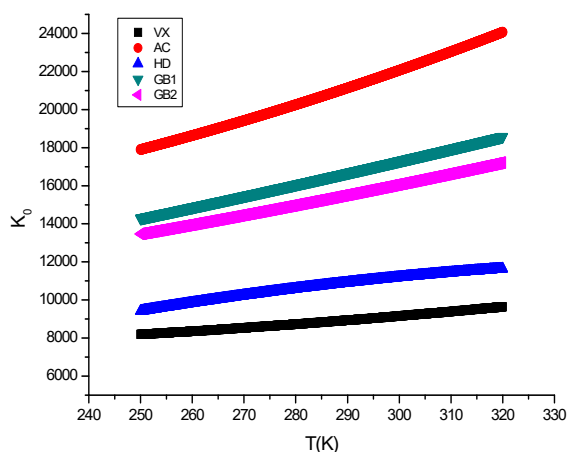## 3. Results and discussions

3.1 CWAs database establishment

Figure 3. K_0 varies with mobility tube temperature T for different CWAs

As shown in Figure 3, four CWAs' K_0 vary with mobility tube temperature linear similarly, the fitting curve between K_0 and T could be expressed as follow equation 4.

$$K_0 = f(T) + b \qquad (4)$$

In equation4, K_0 is mobility ratio and b is intercept. K_0 value is calculated by the equation at any temperature from -25℃ to 45℃. K_0 is a constant when T is determined. Therefore, ion drift time t is also determinate at a certain temperature T. The correlation between t and T is described in Table 1.

Table 1. Correlation between CWAs' t and ion mobility tube temperature-T

CWAs	t=f(T)+b
AC(negative signal)	$1/t = -0.6127 \ast T^2 - 289.82 \ast T + 40089.5$
GB(positive signal)	$1/t = 0.2499 \ast T^2 - 100.84 \ast T + 21412.5$
VX(positive signal)	$1/t = 0.4180 \ast T^2 - 224.98 \ast T + 41822.7$
HD(negative signal)	$1/t = -0.1343 \ast T^2 + 50.39 \ast T - 11245.9$

3.2 CWAs' test

Four kinds of CWAs were tested in high and low concentrations in 25℃, and the result was shown in table 2. Because of limited space, we just take GB test graphs (Figure 4) for an example.

GB attracts cations by its affinity characteristic at room temperature. IMS graph for GB has three peaks; one of these is air peak, and other two for GB1 (monomer) and GB2 (dipolymer) peak (Figure 4). The GB1 monomer peak appears when concentration is low; GB2 dipolymer peak appears when the concentration is high; GB1 monomer peak and GB2 dipolymer peak are all appearing at the same time when the concentration is moderate. GB3 tripolymer peak appears when concentration is extreme high.
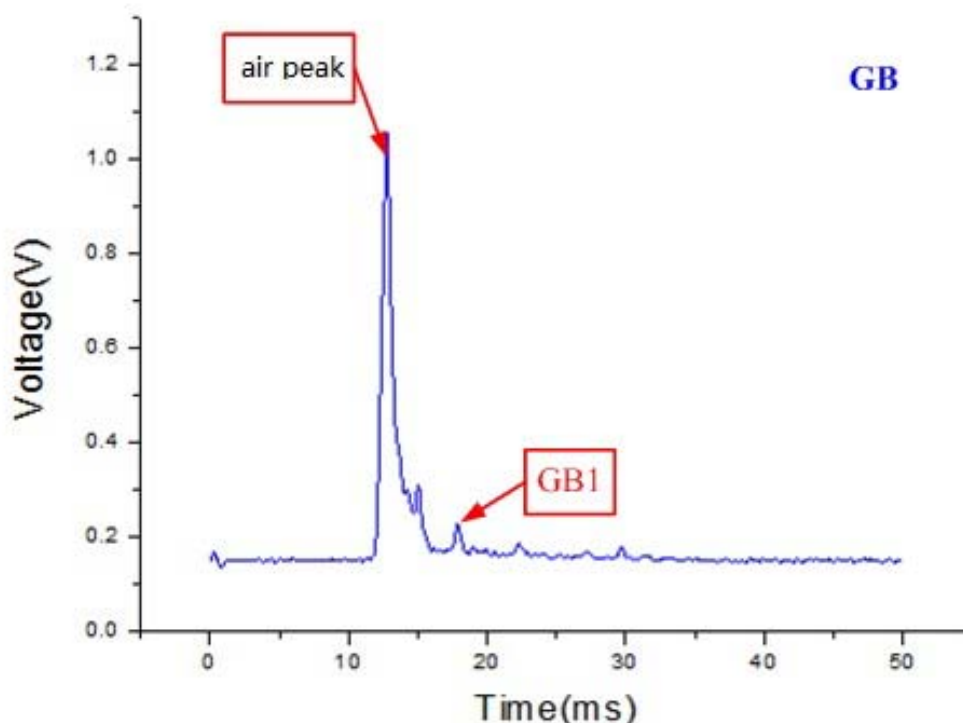

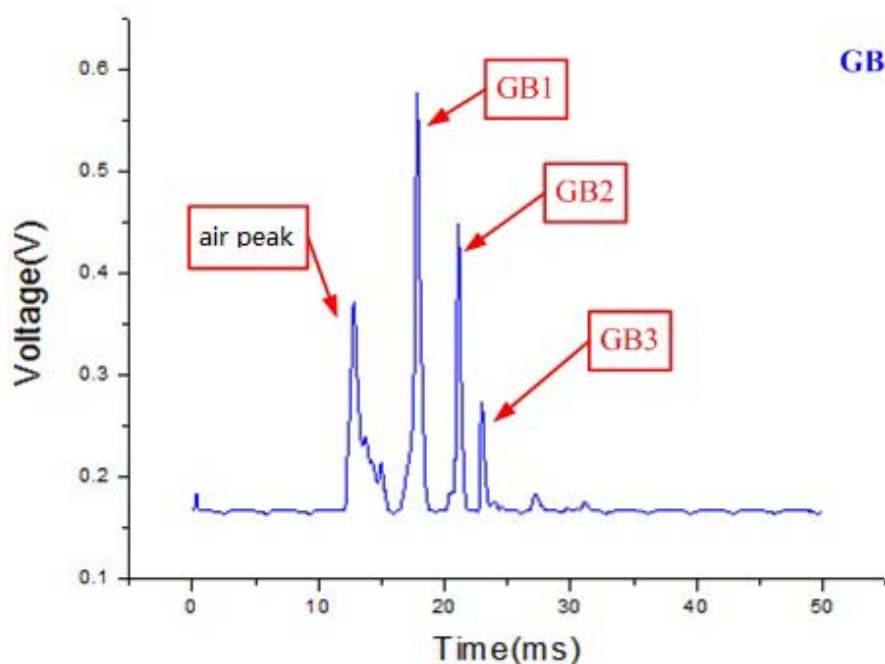Figure 4-a. IMS positive mode signal for 0. 036mg.m^{-3}GB

Figure 4-b. IMS positive mode signal for 9.65 mg. m^{-3}GB

Table 2. CWAs test results

| CWAs | Low concentration test | | | | High concentration test | | | |
	C mg/m^3	tresponse (S)	Amplitude (mV)	Noise (mV)	C mg/m^3	tresponse (S)	Amplitude (V)	Noise (mV)
AC	0.023	6.3	80	15	13.2	4.53	1.98	15
GB	0.036	6.5	100	15	9.65	3.94	1:0.58	15
HD	0.036	12.88	75	15	3.6	5.94	0.78	15
VX	0.024	7.53	85	15	4.58	5.31	1.18	15

From table 2, we can conclude that the IMS instrument has an advantage of higher resolution, quick response (less than 15senconds) and low detection limit. CWAs' peaks can be easily separated from their air background peak on the basis of the tiny difference in mobility time t.

4. Conclusions

From the results above, conclusions could be summarized as follows.

(1) The IMS instrument we developed passed through the high and low temperature tests. Hardware stability has been improved, especially for fast cleaning-up after high concentration test.

(2) Database of correspondence between ion mobility ratio-K_0 and ion mobility tube temperature-T (from -25℃ to 45℃) for GB, VX, HCN and HD has been successfully established.

(3) The IMS instrument responses quickly to 4 CWAs gas mentioned above within 13 seconds at low concentration, less than 6 seconds at high concentration.

(4) The IMS instrument has a low detection limit and a high resolution. 4 CWAs gas could be distinguished easily whenever high or low concentration from each other in air background.

Acknowledgements

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