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RESEARCH PAPER

Quantitative Detection of Hexamethylene Triperoxide Diamine in Complex Matrix by Dopant-assisted Photoionization Ion Mobility Spectrometry

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Abstract: Hexamethylene triperoxide diamine (HMTD), a kind of novel organic peroxide explosives, is often used in terrorist attacks due to its easy synthesis from readily available starting materials. To counteract this new type of threat, a dopant-assisted positive photoionization ion mobility spectrometer was developed on the basis of a nonradioactive ionization source, i.e., vacuum ultraviolet (VUV) lamp, for the determination of HMTD. Toluene, acetone and 2-butanone were tested as dopants, with acetone finally chosen as the optimal dopant for the quantitative detection of HMTD in a perfume matrix. With mass spectrometry, the reactant ions of acetone and the product ions of HMTD were assigned. The reactant ions of acetone were proton dimer $[(CH_3)_2CO]_2H^+$ (*m*/*z* 117), while the product ions of HMTD were proton molecular ion $[HMTD + H]^+$ (*m*/*z* 209). With both the drift tube and the thermal desorber temperature under 120 °C, the HMTD standard samples were quantified with the maximum signal intensity and the 10th second signal intensity, the measurement linear was in the range of 5–50 ng μL^{-1} and 5–100 ng μL^{-1}, and the limit of detection (LOD) was achieved at 0.2 and 0.3 ng μL^{-1}, respectively. Cosmetics such as perfume often interfere and inhibit the measurement of ion mobility spectrometry of the explosives. Therefore, the detection of HMTD in a perfume matrix for the rapid screening and detection of HMTD on-site was of realistic significance. These two quantitative methods were used for the quantitative detection of HMTD in three different brands of perfume samples. By comparison, the method using the 10th second signal intensity of HMTD for the quantitative detection has a better recovery rate and accuracy for HMTD. This method was suitable for the accurate and rapid quantitative detection of HMTD in a complex matrix.

Key Words: Ion mobility spectrometry; Peroxide explosives; Hexamethylene triperoxide diamine; Complex matrix; Perfume

1 Introduction

In recent years, novel organic peroxide explosives such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) were often used in terrorist attacks due to their easy synthesis from readily available starting materials, for example, the Israeli Embassy Bombings in London (1994), the 7 July 2005 London subway bombings, and the 7 August 2006 planned attacks in the United Kingdom. Therefore, an efficient, rapid and reliable on-site detection method for HMTD is urgently needed[1]. As an organic peroxide explosive, HMTD was first synthesized by Legler in 1881 as a white solid powder. The molecular formula was $(CH_2)_6N_2(O_2)_3$, as shown in Fig.1. HMTD is sensitive to metal, shock, friction, and heat[2,3]. However, unlike conventional explosives such as trinitrotoluene (TNT), ammonium nitrate

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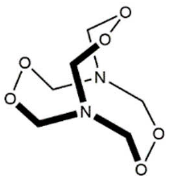

Fig.1 Structure of HMTD

fuel oil (ANFO) and pentaerythritol tetranitrate (PETN), HMTD does not contain nitro groups, aromatic rings, or metal ions in its molecular. Thus, it has no significant absorption band in the ultraviolet region and does not exhibit fluorescence. The analytical methods for conventional explosives are not suitable for the detection of HMTD[4,5].

So far, different techniques have been developed for the detection of HMTD such as infrared (IR)[6,7], Raman[6], mass spectrometry (MS)[8–11], electrical chemical methods[12–14], chemiluminescent[15], high performance liquid chromatography (HPLC)[16], etc. The qualitative analysis of HMTD was performed by IR and Raman, but there were limitations for the quantitative detection of HMTD. In complex matrices, the accurate quantitative detection of HMTD was much more difficult. Although MS can be applied for sensitive detection of HMTD, it is inappropriate for the rapid and on-site detection of HMTD due to its expensive and bulky instruments. The electrochemical and chemiluminescent devices are simple, but they need sample pretreatment and only the degradation product H_2O_2 is analyzed. For HPLC, the sample separation is quite time-consuming, making the on-site detection of HMTD in complex matrices difficult. Therefore, a new method is needed for the rapid, on-site, and accurate quantitative detection of HMTD in complex matrices.

Ion mobility spectrometry (IMS) is a gas-phase ion separation and detection technique. With the attractive features of high sensitivity, rapid response, relative low cost and portability, it was usually used for the detection of trace explosives[17–21], narcotics[22,23], chemical warfare agents (CWAs)[24–27], and volatile organic compounds (VOCs)[28,29]. Conventional nitro explosives, such as TNT, ANFO and PETN with strong electrophilic groups, are usually detected in negative ion mode. In contrast, HMTD is suitable for detection in the positive ion mode due to its high proton affinities with amino groups[5].

So far, there were few related literatures on the detection of HMTD by IMS, where a radioactive ^{63}Ni ionization source was implemented in a few instances[30,31]. Marrs *et al*[32] reported that HMTD could be detected by IMS in both positive and negative ion modes, but the related ion mobility spectrum was not supplied and HMTD was not detected in the complex matrices. Cook *et al*[33] detected HMTD in the presence of four different interferents (two different beverages, moisturizer, and fertilizer) by GC-IMS in the negative ion mode, but the quantitation of HMTD was not given. Therefore, a mature and effective detection method is urgently needed for on-site, rapid, and accurate detection of HMTD in complex matrices.

In this work, with toluene, acetone and 2-butanone as dopants, dopant-assisted positive photoionization ion mobility spectrometry (DAPP-IMS) was used for the determination of HMTD. The reactant ions of acetone and the product ions of HMTD were attributed, and the reaction mechanism between HMTD and reactant ions was also discussed. Furthermore, the thermal desorption properties of HMTD at different thermal desorption temperatures were studied and applied for the quantitation analysis of HMTD in perfume. Owing to the difference in volatility between HMTD and perfume matrix interferents, the two-dimensional desorption separation detection of HMTD in perfume was accomplished. In order to reduce the competition ionization between perfume matrix interferents and HMTD, the signal intensity of HMTD at different thermal desorption times was utilized for the quantitation of HMTD in perfume. As a result, the quantitative accuracy of HMTD in complex matrices was improved.

2 Experimental

2.1 Instrument and apparatus

The schematic diagram of DAPP-IMS in the experiment is shown in Fig.2. The system mainly consisted of a thermal

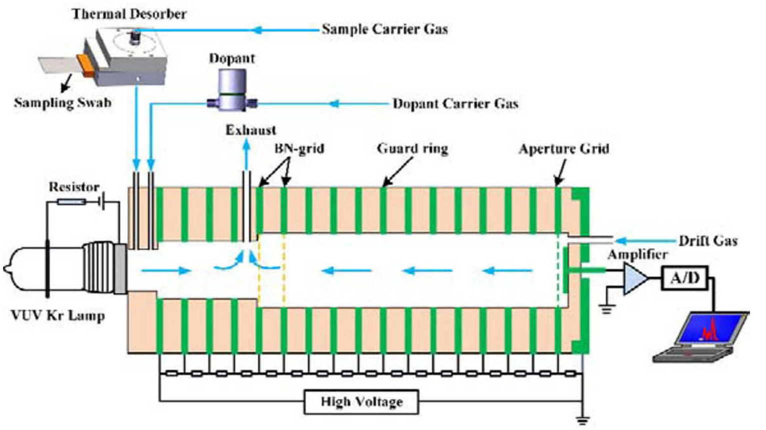

Fig.2 Schematic diagram of dopant-assisted positive photoionization ion mobility spectrometer