



Selectivity improvement of positive photoionization ion mobility spectrometry for rapid detection of organophosphorus pesticides by switching dopant concentration

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ABSTRACT

Ion mobility spectrometry (IMS) opened a potential avenue for the rapid detection of organophosphorus pesticides (OPPs), though an improved selectivity of stand-alone IMS was still in high demand. In this study, a stand-alone positive photoionization ion mobility spectrometry (PP-IMS) apparatus was constructed for the rapid detection of OPPs with acetone as dopant. The photoionization of acetone molecules was induced by the ultraviolet irradiation to produce the reactant ions $(Ac)_2H^+$, which were employed to ionize the OPPs including fenthion, imidan, phosphamidon, dursban, dimethoate and isocarbophos *via* the proton transfer reaction. Due to the difference in proton affinity, the tested OPPs exhibited the different dopant-dependent manners. Based on this observation, the switching of dopant concentration was implemented to improve the selectivity of PP-IMS for OPPs detection. For instance, a mixture of fenthion, dursban and dimethoate was tested. By switching the concentration of doped acetone from 0.07 to 2.33 to 19.94 mg L⁻¹, the ion peaks of fenthion and dursban were inhibited in succession, achieving the selective detection of dimethoate at last. In addition, another mixture of imidan and phosphamidon was initially detected by PP-IMS with a dose of 0.07 mg L⁻¹ acetone, indicating that their ion peaks were severely overlapped; when the concentration of doped acetone was switched to 19.94 mg L⁻¹, the inhibition of imidan signals promised the accurate identification of phosphamidon in mixture. Finally, the PP-IMS in combination of switching dopant concentration was applied to detect the mixed fenthion, dursban and dimethoate in Chinese cabbage, demonstrating the applicability of proposed method to real samples.

1. Introduction

The group of organophosphorus pesticides (OPPs) is one of the widely-used classes of pesticides to increase the agricultural productivity. However, their extensive use also increases the pesticide residues in soil, water and agricultural products, which are harmful to human health due to their toxicity as well as the potential mutagenic and carcinogenic properties [1]. Therefore, the development of increasingly simple, rapid and sensitive methods for the detection of OPPs residues is necessary.

At present, the chromatographic methods are the most commonly-used analytical methods for the detection of OPPs, such as gas chromatography (GC) with nitrogen-phosphorus detector [2,3], flame

photometric detector [4] and mass spectrometer [5,6], and high performance liquid chromatography (HPLC) with ultraviolet detector [7], photodiode array detector [8] and mass spectrometer [9,10]. Due to the high separation power of chromatography, these methods can be readily used for the selective detection of OPPs. Whereas, the time duration for OPPs analysis by chromatographic method usually requires a few minutes, suggesting that chromatographic method is not so practical to provide a timely result of OPPs detection. In some fields of pesticides monitoring, such as food safety monitoring, a simple and rapid analytical method is required so much, because sometimes the food safety officers do need such a test result of pesticides residues within a very short period of time, in order to make a suitable safety evaluation for the tested food.

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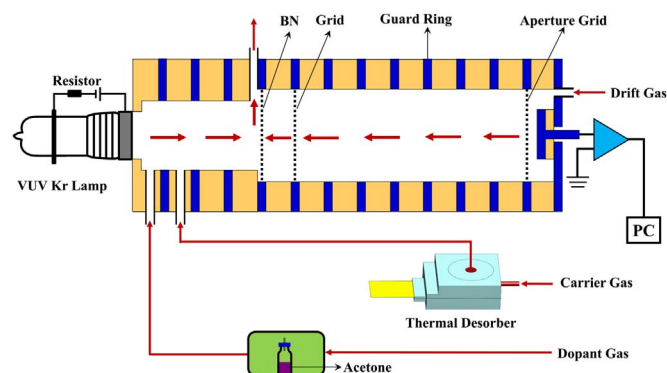


Fig. 1. Schematic drawing of the positive photoionization ion mobility spectrometry (PP-IMS) with acetone as dopant.

Table 1
Operating conditions of PP-IMS.

Operating condition	Setting
Ion source	Kr lamp (10.6 eV)
Operating mode	Positive
Temperature of IMS cell	120 °C
Drift field	389 V cm ⁻¹
Flow rate of carrier gas	300 mL min ⁻¹
Flow rate of drift gas	400 mL min ⁻¹
Flow rate of dopant gas	100 mL min ⁻¹

Ion mobility spectrometry (IMS) is a well-known technique for the separation and detection of gaseous ions in a weak electric field, based on the differences of ion mobility at the atmospheric pressure. Owing to the fast analysis, high sensitivity and good portability, IMS has been successfully applied in the rapid detection of explosives, illicit drugs and toxic industrial chemicals [11–17]. Moreover, IMS has afforded a potential tool for the rapid detection of OPPs in recent years [18–24]. For instance, Jafari et al. [19] employed the positive ⁶³Ni ionization IMS to detect malathion, ethion and dichlorovos, and the limits of quantification reached ng level. Ebrahimi et al. [22] combined the negative corona discharge ionization IMS with the dispersive liquid-liquid microextraction for the analysis of ethion, and the feasibility of this method was verified by its application to real samples. However, the resolving power of a stand-alone IMS is relatively low, making it difficult to resolve the ion peaks of OPPs with slight differences in ion mobility [18,19,23]. To improve the selectivity of IMS for OPPs detection, GC method was commonly-combined to pre-separate the target OPPs [21,23]. Saraji et al. [23] combined the corona discharge ion mobility spectrometry with GC separation, accomplishing the selective detection of diazinon, parathion and fenthion which exhibited the overlapped ion peaks on the ion mobility spectra. Whereas, the combination of GC separation would increase the analysis time to a dozen of minutes, blocking the application of IMS method in the rapid detection of OPPs in practice. Hence, it is desirable to develop a simple and rapid method to improve the selectivity of IMS for OPPs detection.

In this study, a stand-alone positive photoionization IMS (PP-IMS) apparatus was designed for the rapid detection of OPPs with acetone as dopant. The switching of dopant concentration was implemented as a

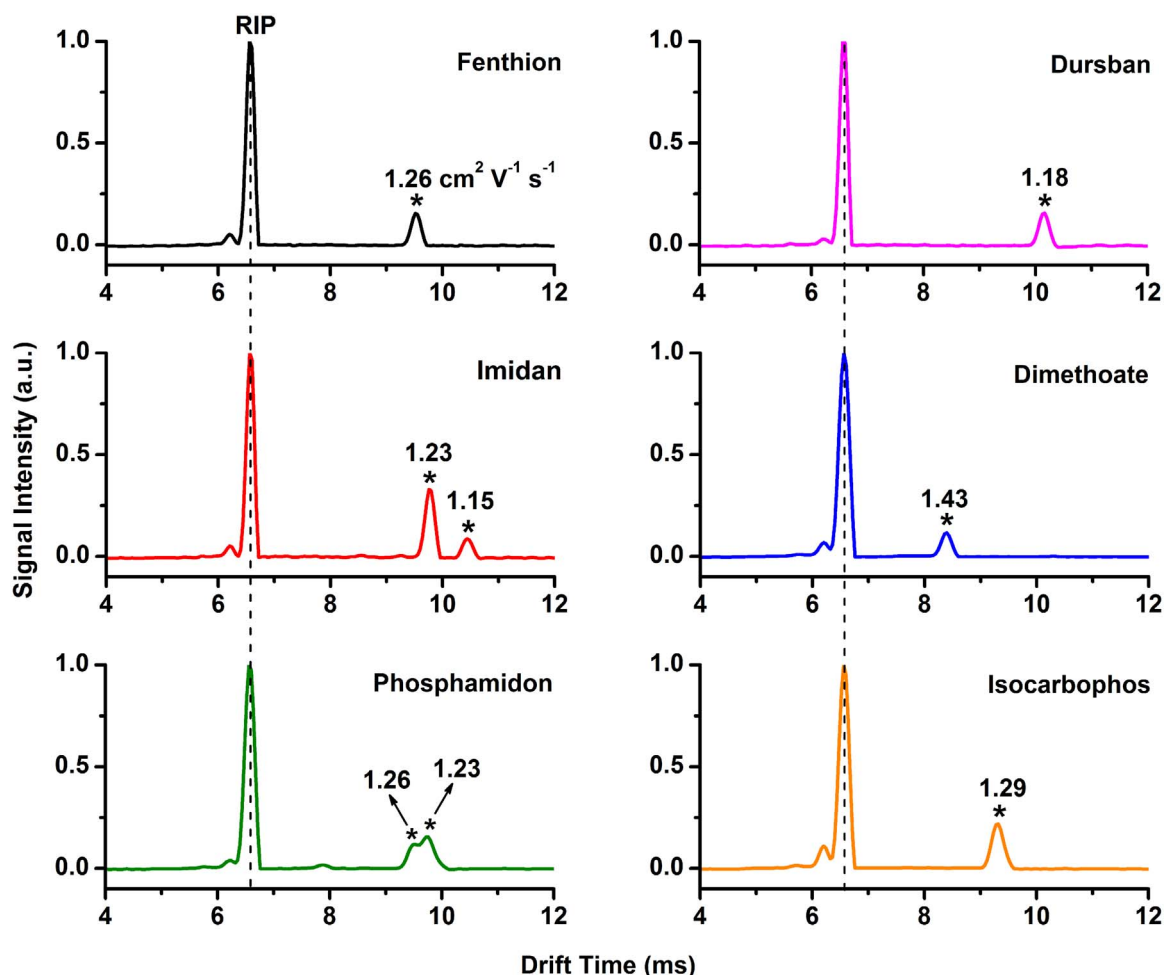


Fig. 2. Ion mobility spectra of fenthion, imidan, phosphamidon, dursban, dimethoate and isocarbophos by PP-IMS with acetone as dopant.

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