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Short communication

Determination and identification of malathion, ethion and dichlorovos using ion mobility spectrometry

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Abstract

Positive ion mobility spectra of different organophosphorus pesticides such as malathion (*s*-(1,2-dicarb-ethoxyethyl) *o*,*o*-dimethyl dithiophosphate), ethion (*o*,*o*,*o*′,*o*′-tetraethyl *s*,*s*′-methylene bis(phosphorodithioate)) and dichlorovos (2,2-dichlorovinyl dimethyl phosphate) have been studied in air at ambient pressure using ion mobility spectrometry method with ^{63}Ni ionization source. The limits of quantification (LOQs) were 1.0×10^{-9}, 1.0×10^{-9} and 5.0×10^{-9} g for malathion, ethion and dichlorovos, respectively. The working range of these compounds was about three orders of magnitude and the relative standard deviation (R.S.D.) of repeatability at the 5 μg ml^{-1} level were all below 15%. Furthermore, in this study, the influences of IMS cell temperature on the ion mobility spectra of these compounds were investigated.

Keywords: Malathion; Ethion; Dichlorovos; Ion mobility spectrometry

1. Introduction

1.1. Summary of pesticides analysis

Pesticide intoxications are widely occurred in agriculture, especially in the developing countries. Pesticide poisonings are known to be a major public health problem. For this reason, there are approximately 220,000 deaths per year on a worldwide scale. Therefore rapid, simple and sensitive field methods are required to check the presence of these compounds [1].

Organophosphorus compounds (OPCs) are the major group of the pesticides. So far, traditional methods such as: gas chromatography (GC) with different detectors [2–4], high performance liquid chromatography with UV detection (HPLC-UV) [5,6] and biosensors [7] have been used for analysis of these compounds. However, these methods are known to be expensive and quite laborious [8–10]. Ion mobility spectrometry (IMS) has been proven to be one of the best methods for the detection of trace level of OPCs [1,11–13].

Ion mobility spectrometry (IMS) is an instrumental method in which two independent principles are combined to provide high speed response to trace levels of chemicals as gas or vapor species [14–17]. In IMS, sample vapors are converted to ions at atmospheric pressure and those ions are characterized by their gas phase mobilities in weak electric fields [18,19]. Early instruments for IMS exhibited picogram detection limits without sample preconcentration and generated strong interest in the technique. Organophosphorus compounds have high proton affinities and therefore readily produce positive ions in the reaction region of the ion mobility spectrometer, even in the presence of several other constituents present in ambient air [20].

1.2. Summary of IMS principles

Standard IMS instrumentation is comprised of four major sub-components: an ion source region, an ion gate, a drift region and a detector [20]. Typically, the ion source has been 10 mCi of ^{63}Ni-foil. Using such a source, one can produce reactant ions (background ions) from nitrogen gas according to this reaction: $N_2 + \beta^- \rightarrow N_2{}^+ + \beta'^- + e^-$, where β^- is the beta particle from the ^{63}Ni source and β'^- is the beta particle after some of its energy has been used in ionization of the nitrogen molecule. The primary $N_2{}^+$ is too short-lived to appear in the mobility spectrum, but it begins a series of ion-molecule reactions with trace amounts of H_2O or NH_3 in the drift gas [20]. Therefore the

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reactant ions of $(H_2O)H^+$ or NH_4^+ can be formed and finally, the product ions of sample might be produced from proton transfer reactions between analyte and reactant ions. The other sources such as corona discharge [21], electrospray [22] and photoionization [23] have been demonstrated as ionization source for IMS. The purpose of an ion-gate is to electronically inject ions, as a discrete packet, from the ion source region into the drift region. In the drift region, an electric field (about $200\,\mathrm{V\,cm^{-1}}$) is established using a voltage divider and a series of conducting rings stacked between the ion gate and the detector. Ions under the influence of this electric field move toward the detector, nominally a Faraday plate, and create a signal (i.e. current flow) through collisional neutralization at the detector [24–26]. The output of the amplified signal is synchronized to the gate pulse yielding a mobility spectrum, a plot of ion current versus time of ion drift. Ionization of sample occurs via atmospheric pressure chemical ionization (APCI) reactions between the sample vapors and a reservoir of charge called the reactant ions [27,28]. Pesticides possess relatively high electron and proton affinity groups in the gas phase and are best observed as negative and positive ions [20]. In the positive mode of IMS, the analyte is ionized in ion-molecular exchange reactions with reactant ions, which are commonly hydrated protons. The reactant ions in negative polarity are thermalized electrons in nitrogen and are hydrated O_2 or CO_2 with air. Other reactant ions such as ammonium, protonated acetone and halides, have also been used as alternative reagent ions for enhancing sensitivity and selectivity of the method [29]. Therefore in order to enhance sensitivity and remove background interferences, reagent gases may be used to create alternate reactant ions that provide additional selectivity in response.

2. Experimental

2.1. Instrumentation

Ion mobility spectrometer used in this work has been made in Engineering Research Center of Isfahan by Detector Group. IMS cell with 17 cm long was made from 15 stainless steel rings with 2.8 cm inner diameter that separated from each other by thin PTFE sheets. The schematic diagram of the apparatus is as the same with that shown by Hill et al. [30]. A ^{63}Ni-foil of 12 mCi was used as an ionization source in this cell. The rings were connected by a series of resistors to form the electric field. A flow of air as drift gas was introduced to end of the cell, near the detector. The injection port was a T-shape union made of brass alloy. The carrier gas passes through the port and carries the analyte vapor to the IMS cell. The injection port was equipped with a heating element and a digital temperature controller (Lae, Italy). A small steel cap was used to introduce samples. The sample solutions were placed on the cap and after evaporating the solvent, the cap was inserted into the injection port. A flow of air carrier gas was used for introducing of sample vapor to ionization source. The gas was filtered with a 13× molecular sieves (Fluka) trap before it entered the IMS in order to remove water vapor or other contamination. The optimum experimental conditions for obtaining the ion mobility spectra of the compounds are shown in Table 1.

Table 1
Optimum experimental conditions

Parameter	Setting
Length of drift tube	8.0 cm
Applied field	250 V cm
Drift gas (air)	600 ml/min
Carrier gas (air)	350 ml/min
Drift temperature	150 °C
Injection temperature	140 °C
Pressure	630 Torr
Gate width	200 μs
Reactant gas	Acetone

2.2. Chemicals and solutions

The chemical solvent (acetone) used in this work was obtained from Merck. Commercial-grade organophophorus pesticides (malathion, ethion and dichlorovos) were obtained from Plant Protection Organization (Tehran). Stock standard solutions (50 ppm) of these compounds were prepared in acetone and then working solutions were made by successive dilution of the stock solutions.

3. Results and discussion

3.1. Cell temperature effect on spectrum

It is very important that why the optimum cell temperature has been chosen 150 °C. Therefore in this work, the influence of IMS cell temperature on the malathion, ethion and dichlorovos spectra was investigated. The results of these studies are shown in Fig. 1. According to this figure, increasing the cell temperature changes the number of peaks at all of the spectra. This behavior is due to decomposition of the pesticides at high temperatures as same as for explosives in our previous work [21]. At low temperatures, acquisition time (from the injection time until the sample peaks disappear) is increased and as a result, analysis duration of the sample is become longer. Therefore, selecting of suitable cell temperatures is very important for analysis of the compounds. The optimum IMS cell temperature for malathion, ethion and dichlorovos was 150 °C.

3.2. Quantitative analysis

The ion mobility spectra of background and 2.0×10^{-8} g of malathion, ethion and dichlorovos are shown in Fig. 2. These spectra were obtained at the optimum conditions of IMS (Table 1). In this work, acetone was used as a reagent gas to create alternate reactant ion that provide additional selectivity in response. Protonated acetone ion is the reactant ion (RI), which can be distinguished from the background spectrum. The high proton affinity of acetone with respect to water is helpful in eliminating the ion clusters of $(H_2O)_nH^+$. This phenomenon is shown in Fig. 3. The ion mobility spectrum of malathion shows one peak labeled M. The ethion and dichlorovos spectra show two peaks (E_1, E_2) and three peaks (D_1, D_2 and D_3), respectively. The reduced mobility values of all of these ions are shown in Table 2. In fact, the recognition of the ions with confidence requires coupling of IMS with a mass spectrometer.

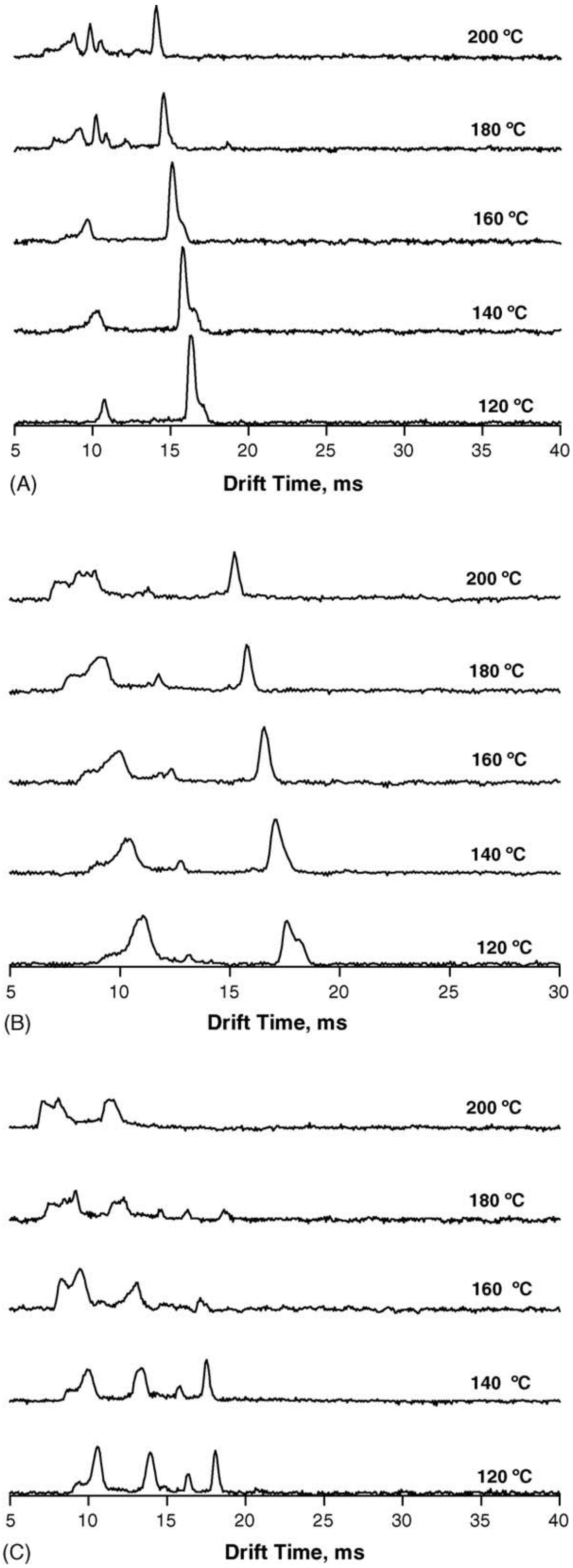

Fig. 1. The ion mobility spectra at different cell temperatures for (A) malathion, (B) ethion and (C) dichlorovos.

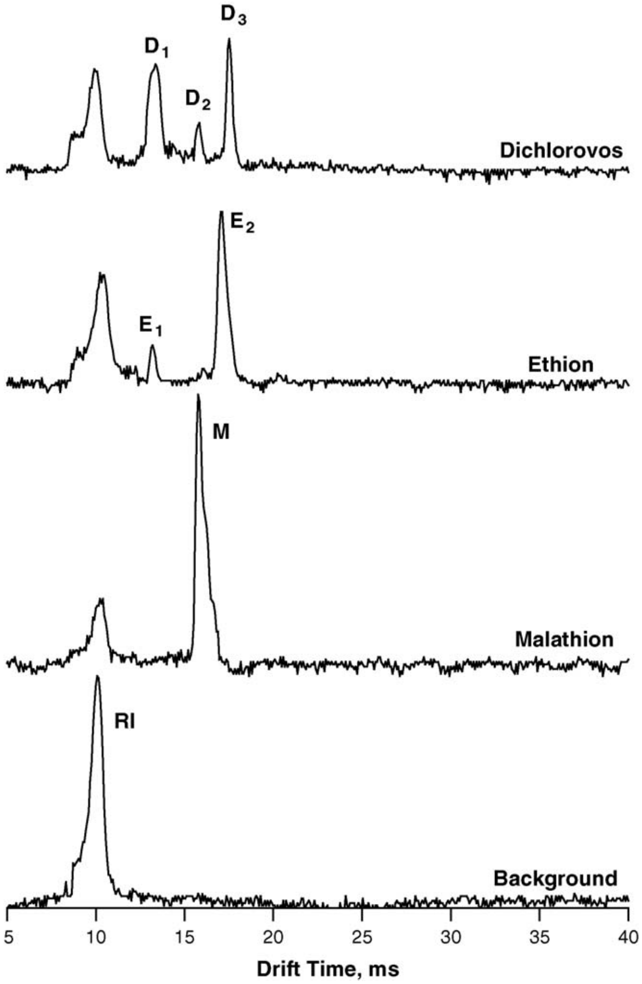

Fig. 2. The ion mobility spectra of the background, malathion, ethion and dichlorovos.

When the sample, 10 ml, was placed on the cap and after evaporating the solvent, the cap was inserted into the injection port the signal appears after a short time, reaches a maximum and decays almost exponentially. It was noticed that during the acquisition time the relative peak area is changed. The sum of the areas of peaks (total) against the acquisition time, obtained by exposure to varying concentrations of malathion, is shown in Fig. 4. The integration of this plot was considered as the response. The IMS responses for ethion

Table 2
Characteristic ions for organophosphorus compounds ion mobility spectra

Peak	Reduced mobility, K_0 (cm^2 V^{-1} s^{-1})	Drift time, t (ms)
RI	2.03 ± 0.09	10.08
M	1.30 ± 0.06	15.76
E_1	1.55 ± 0.08	13.20
E_2	1.20 ± 0.05	17.12
D_1	1.53 ± 0.07	13.36
D_2	1.29 ± 0.06	15.84
D_3	1.17 ± 0.04	17.52

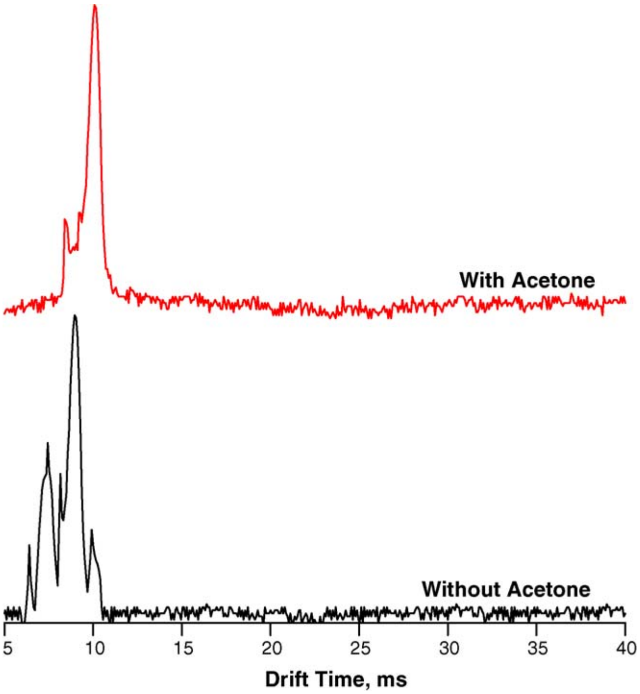

Fig. 3. Comparison of the ion mobility spectra of background with and without acetone.

and dichlorovos were calculated as the same with that of the malathion.

The calibration curves for the malathion, ethion and dichlorovos were obtained by plotting their respective responses against the amount of each compound. These calibration curves are shown in Fig. 5. The linear ranges were 1.0×10^{-9} to 1.0×10^{-7}, 1.0×10^{-9} to 5.0×10^{-8} and 5.0×10^{-9} to 1.0×10^{-7} g for malathion, ethion and dichlorovos, respectively. The working range is about three orders of magnitude for these compounds. Detection limits (LODs) of this method for determination of malathion, ethion and dichlorovos are 2.1×10^{-10},

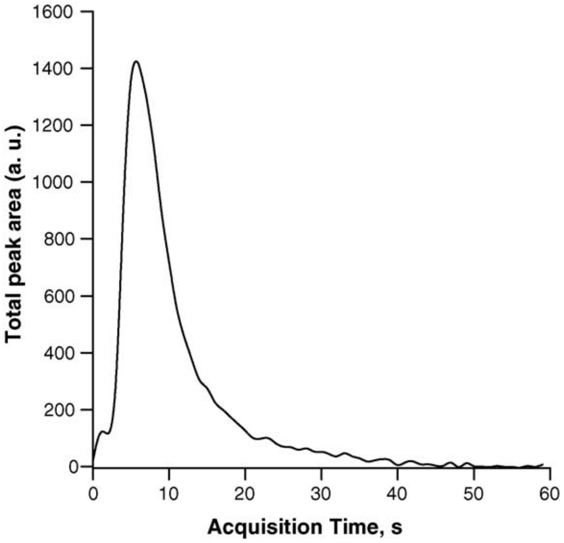

Fig. 4. The sum of the areas of peaks (total) against the acquisition time obtained by exposure to amount of 2.0×10^{-8} g of malathion.

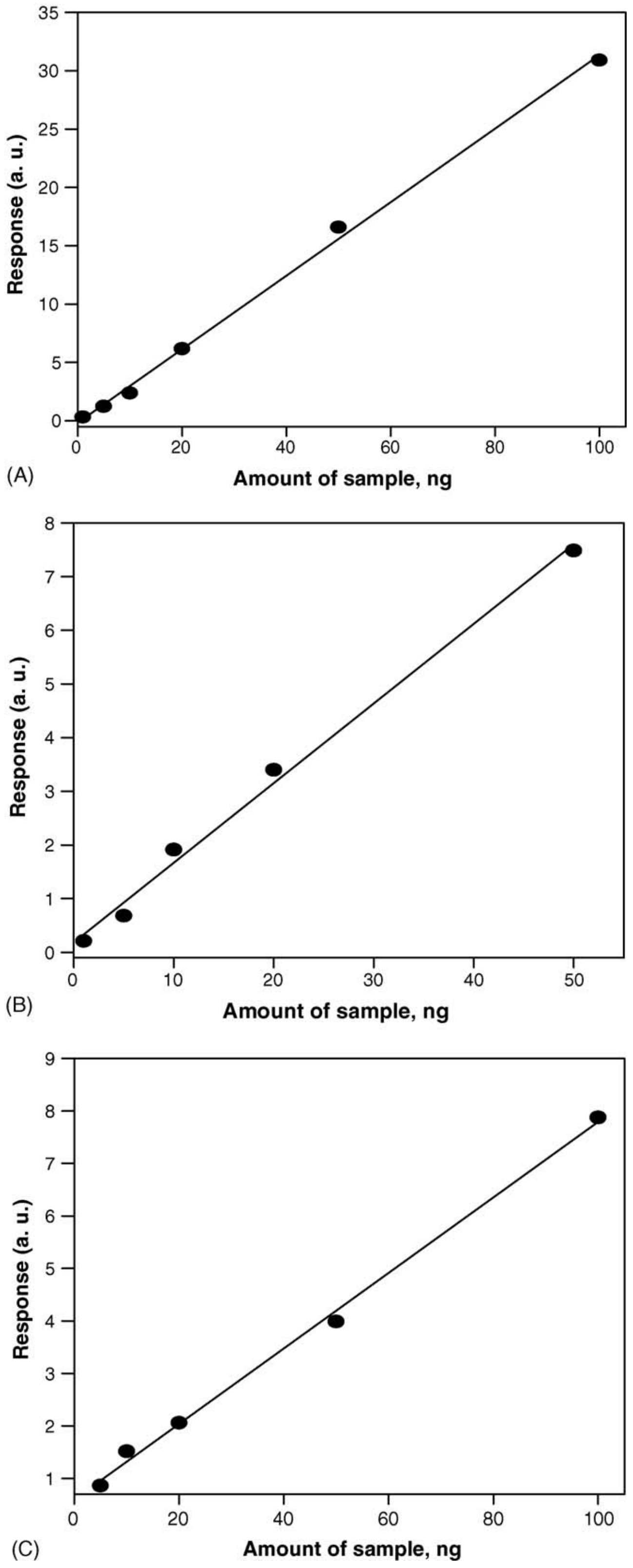

Fig. 5. Plots of IMS response against the amount of (A) malathion, (B) ethion and (C) dichlorovos.

Table 3
Linear range, limit of detection (LOD) and repeatability ($n = 10$) of three organophosphorus pesticides

Compound	Formula	R^2	Linear range (g)	LOD (g)	R.S.D. (%)
Malathion	$y = 3.15x - 0.17$	0.9977	1.0×10^{-9} to 1.0×10^{-7}	2.1×10^{-10}	12.5
Ethion	$y = 1.48x + 0.19$	0.9939	1.0×10^{-9} to 5.0×10^{-8}	4.5×10^{-10}	10.1
Dichlorovos	$y = 0.72x + 0.60$	0.9969	5.0×10^{-9} to 1.0×10^{-7}	9.4×10^{-10}	14.9

4.5×10^{-10} and 9.4×10^{-10} g, respectively. The relative standard deviation percentage (R.S.D.%) was found to be typically below 15% and the correlation coefficients (R^2) were above 0.99 (Table 3).

4. Conclusions

IMS is a separation technique that affords qualitative and quantitative information associated with the analysis of chemicals. Ion mobility has the very low response time (∼5 s) and detection limit (pg). Furthermore the portable IMS can be achieved easily. The results reveal that the ion mobility spectrometer can be used to detect and identify some of the pesticides compounds. Therefore a portable IMS can be made for detection and identification of trace residue pesticides in foods. This will be very useful for human health.

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