FAST AND SIMPLE IDENTIFICATION AND MEASUREMENT OF PHOSALONE USING ION MOBILITY SPECTROSCOPY

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ABSTRACT

Phosalone is a chemical compound used as a pesticide in agriculture and horticulture. Phosalone can be identified and measured with different devices in all kinds of agricultural and horticultural products. Despite the various methods of spectroscopy with various applications in the fields of chemistry and physics, it can be used to identify and measure a variety of chemical compounds. But the ion mobility spectrometer is a simple, low-cost method that does not require complex extraction methods to identify and measure organic compounds. With this research, the possibility of measuring Phosalone pesticide by ion mobility spectrometer in positive polarity was investigated. This test was performed without the need for complicated sample preparation steps. At first, the Phosalone standard sample was identified by the IMS device and the optimal conditions for its measurement were determined. The data was analyzed with SigmaPlot software. The optimal temperature of the tube was 200°C and the optimal temperature of the injection chamber was 260°C. The linear range for measuring Phosalone ppm was determined to be 0.5-20. The detection limit of 1.4 ppm and determination limit of 4.7 ppm was obtained.

Keywords: Phosalone, ion mobility spectrometer, detection, measurement, optimization, detection limit and determination limit

INTRODUCTION

The world's population is expanding, which makes the need for food more pressing[1, 2]. It is essential and important to increase and sustain agricultural and food output in the near future

[1, 3, 4]. Among these are compounds that shorten the shelf life of agricultural and food items. Plant pesticides are one of the main things that lower food[5, 6].

Chemical or non-chemical substances known as pesticides are used to eradicate or manage a variety of pests and nuisance organisms, including animals, plants, fungi, weeds, and aquatic creatures as well as bacteria, viruses, and microbes[7, 8]. These chemicals kill plant pests but also severely harm agricultural crops [6, 9, 10]. The aforementioned article states that because pesticides have the ability to produce goods that are not hazardous to human health, several studies have been carried out to evaluate, extract, identify, and quantify them. For testing organic molecules, an ion mobility spectrometer is an appropriate, straightforward, and affordable tool [11, 12]. An organophosphorus insecticide called Phosalone is used in agriculture and horticulture to get rid of several plant pests[13]. Overuse of Phosalone has a negative impact on human and other living things' health. The purpose of this study is to present a low-cost, straightforward technique for measuring and identifying the pesticide Phosalone without the need for intricate extraction and separation procedures. The ion mobility spectrometer is a valuable method for identifying and measuring organic compounds, and especially for measuring and identifying agricultural pesticides and food. Fusalon residues in agricultural products are also harmful to humans, and how identifying these residual pesticides in fruits and vegetables requires comprehensive research on various laboratory devices. And how to test the pesticides in the device and how to optimize the devices, in this sense, this research is an urgent need. The ion mobility spectrometer device used in this research was made in Isfahan University, Iran, by Taf Technology Company[12, 14].

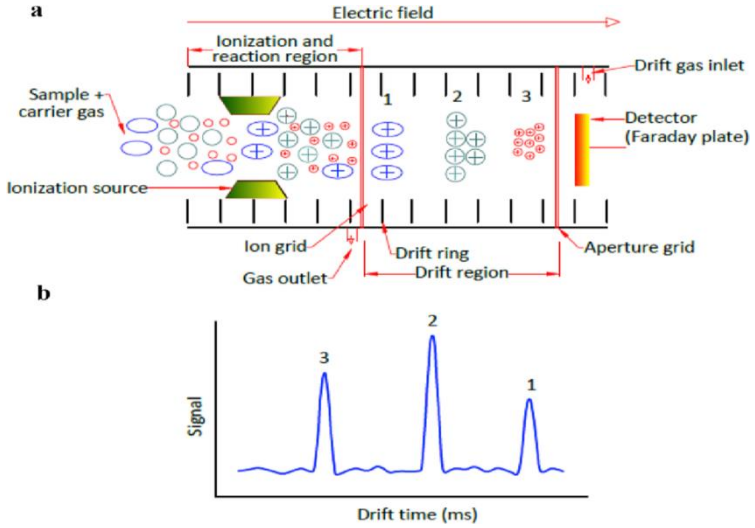
In the sample preparation and analysis section, the various methods introduced in scientific sources for pesticide analysis show the importance of this issue at the world level [15-17]. Sample preparation can be considered as one of the most important stages of pesticide measurement, which includes sample pre-concentration and cleaning[18, 19]. In most cases, sample preparation is necessary for the analysis of various chemical compounds in complex tissues So far, various sample preparation technologies include liquid-liquid extraction (LLE), solid phase extraction (SPE), hanging drop micro extraction (SDME), solid phase micro extraction (SPME) and liquid phase micro extraction (LPME), have been presented

Chromatographic methods require long times for separation in the column, which leads to a decrease in the speed of the analysis flow [13, 20, 21]. In addition, one of the main requirements of HPLC is the use of high-purity washing solvents. On the other hand, identification methods by GC are limited to the analysis of volatile compounds or require

time-consuming and laborious derivatization methods before sample analysis. Additionally, IMS doesn't require a vacuum system like MS does. This device's mobility, fast reaction time, great sensitivity, and simplicity of use are further benefits[13]. Analyzing genuine samples with intricate textures is one of the IMS device's issues, particularly when analyzing real samples

Liquid-liquid micro extraction and negative corona discharge ionization have been integrated for the purpose of detecting and measuring pesticides[22, 23]. The practical application of the suggested technology has demonstrated its efficacy.

The ion mobility spectrometer device consists of four main parts, including the detector, the drift region of the ion source, and the ion grid[24, 25]. Carrying out chemical reactions of the sample with reactant ions (in positive polarity) or electrons (in negative polarity) in the ionization region, turns the sample vapors into desired ions[26]. The pulse injection of ions from the ionization zone to the thrust zone is done through the ion network. Ions move to the drift region under the influence of the applied electric field and hit the detector at different times based on the difference in size and mass. The signal resulting from the impact of the ions on the detector, after being amplified with the help of an amplifier, creates the ion mobility spectrum. Figure (1. a and b) shows the principle of operation of the ion motion spectrometer. The ion source is one of the main and important parts of the IMS device. In order to ionize the sample molecules in the IMS device, different ionization sources can be used[11, 27]



Figure(1) Schematic of ion mobility spectrometer[28]

Materials and methods

1- Solubilization of Phosalone

In this research, Phosalone of Merck company was used, 10 mg of Phosalone powder was weighed and transferred to a 100 ml flask and made up to 100 ml with methanol. A solution of 100 ppm Phosalone was prepared and to measure Phosalone by an ion mobility spectrometer under different conditions, one microliter was injected into the device with a 10 microliter Hamilton syringe, and its ion mobility spectrum was recorded..

2. Phosalone injection and recording peaks

In this practical work, the input gas to the ion mobility spectrometer to produce interacting ions is compressed air. The interacting ions in the ionization region and the presence of air thrust gas include (H2O)nH+, NH4+(H2O)n and NO+(H2O)n.

The first peak at 4 milliseconds corresponds to protonated ammonia. The second peak at 4.6 milliseconds corresponds to NO+ and the third peak at 5.2 milliseconds corresponds to H3O+ ions (protonated water vapor).

In the ionization zone, Phosalone molecules take protons from interacting ions and become ions. Phosalone ions enter the thrust area of the IMS device from the electrical network in a pulsed manner and move under the influence of an electric field of about 500 V/cm and reach the detector in 12.5 milliseconds.

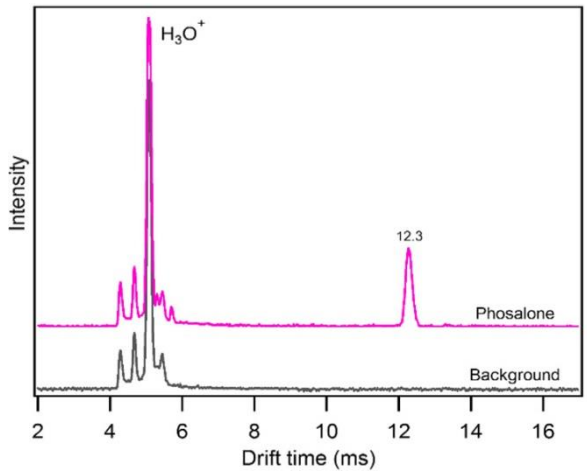


Figure (2) background and the peak of Phosalone to the ion mobility spectrometer injection at 200 C temperature

3- The temperature of the thrust tube and the injection chamber to measure Phosalone

As can be seen in Figure (3), with the increase in the temperature of the cell, the peaks of Phosalone are shifted to a shorter time and its intensity increases. Finally, the peak intensity

of Phosalone has increased at high temperatures, so the temperature of 200°C was chosen as the optimal temperature for measuring Phosalone. In figure (4), the maximum peak intensity of Phosalone at each temperature is plotted in terms of temperature.

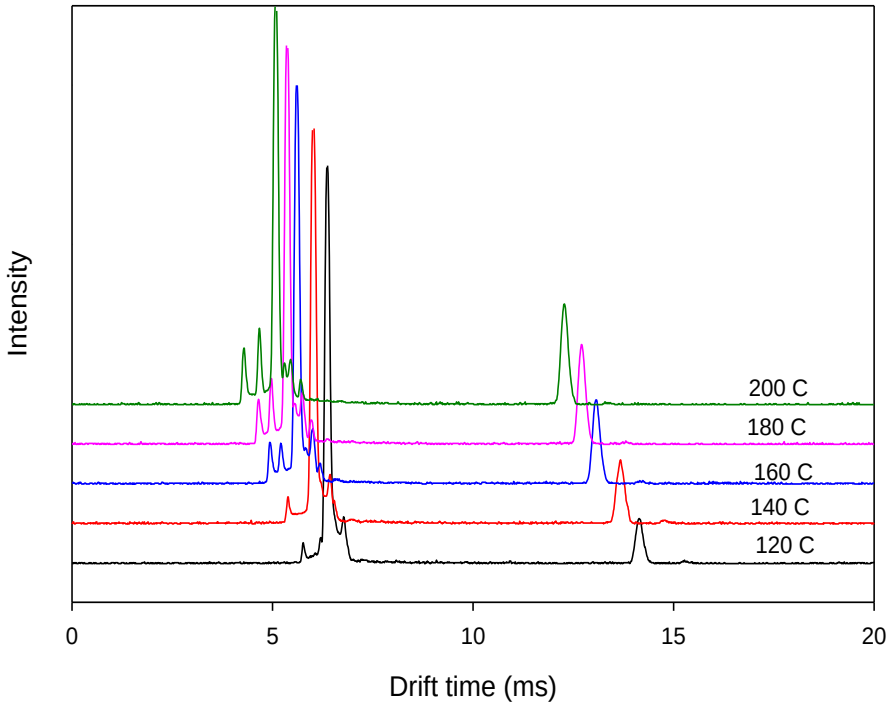


Figure (3) Ion mobility spectrum resulting from the injection of two microliters of 100 ppm Phosalone at different temperatures of the thrust tube

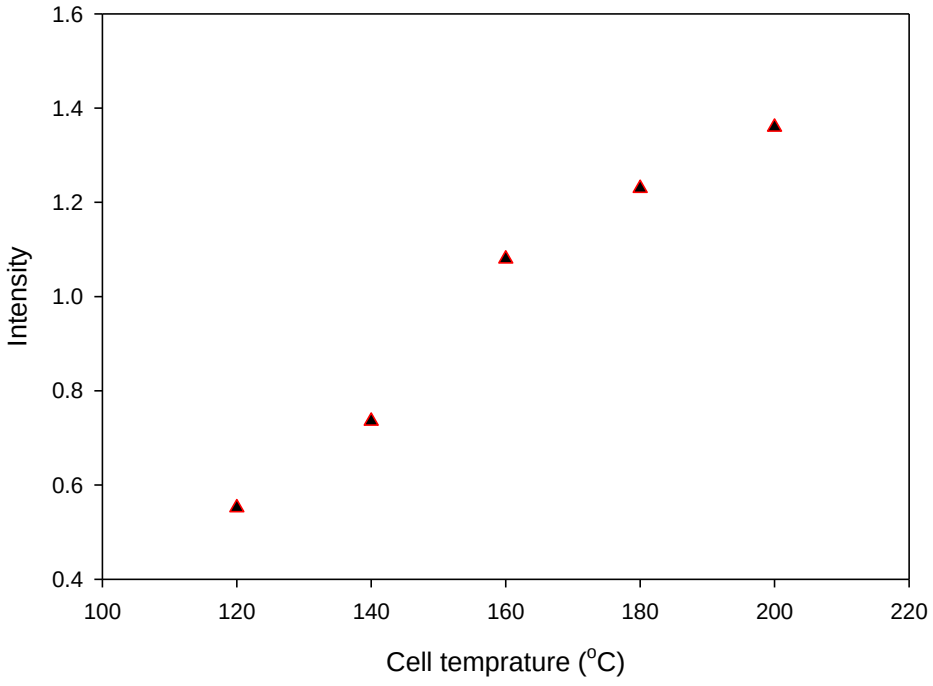


Figure (4) The maximum intensity of Phosalone signal at each temperature according to the temperature of the thrust tube

To check the temperature of the injection area, two microliters of 100 ppm Phosalone solution were injected into the device at different temperatures of the injection area and the optimum temperature of the cell (200 degrees Celsius) and their spectrum was recorded as seen in Figure (5) with Increasing the temperature of the injection area, the peak intensity of Phosalone increased. The temperature of 260 °C was obtained as the optimal temperature. In fact, the increase in the intensity of the Phosalone signal can be attributed to the increase in its evaporation rate and the increase in the sample input to the ionization zone. Other optimized parameters are listed in Table (1).

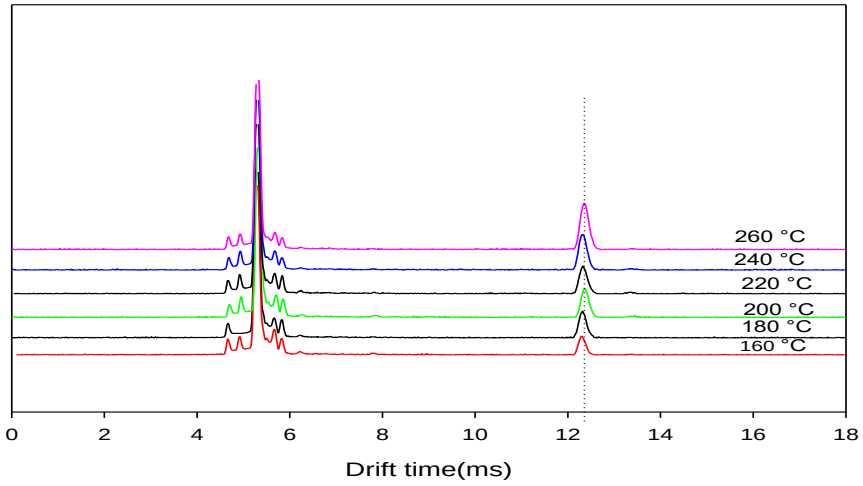


Figure (5) ionic mobility spectrum of Phosalone at different temperatures of the injection chamber

Table (1) optimal parameters of the ion mobility spectrometer device for the measurement of Phosalone

parameter	Settings
Corona voltage	2300 V
Thrust area voltage	8000 V
Thrust tube field	500V/cm
Buoyancy gas flow rate (compressed air)	600 ml/min
Carrier gas speed (compressed air)	300 ml/min
The temperature of the injection chamber is	260 °C

The temperature of the thrust tube is	200 °C
Pulse width	50 μs
device polarity	Positive

research findings

4- Calibration curve and figures of merit

In order to obtain the calibration curve, different concentrations of Phosalone 0.5-100 ppm were prepared in methanol solvent. Then, in the optimal conditions obtained for the measurement of Phosalone (Table 1), the amount of two microliters of different concentrations of Phosalone was injected three times into the IMS device and their spectrum was recorded.

To obtain the calibration curve, the area under the peak was plotted against the concentration. Figure (5) shows the calibration curve of Phosalone. In this graph, the Y-axis is the sub-peak level and the X-axis is the concentration of Phosalone. In the line equation y=ax+b, a is the slope of the calibration curve and b is the width from the origin. In Figure (6), there is a linear range (0.5-20 ppm) and a saturation range. In the linear range of Figure (7), with increasing concentration, the area under the peak increases linearly. Therefore, its line equation can be obtained. In the saturation range, the level below the peak does not change with increasing concentration. In fact, the maximum signal that the device can show does not increase from the saturation concentration onwards.

In quantitative and accurate measurement, the linear range of the calibration graph is important because the area under the peak indicates the specific concentration. By obtaining the linear equation, the unknown concentration can be calculated.

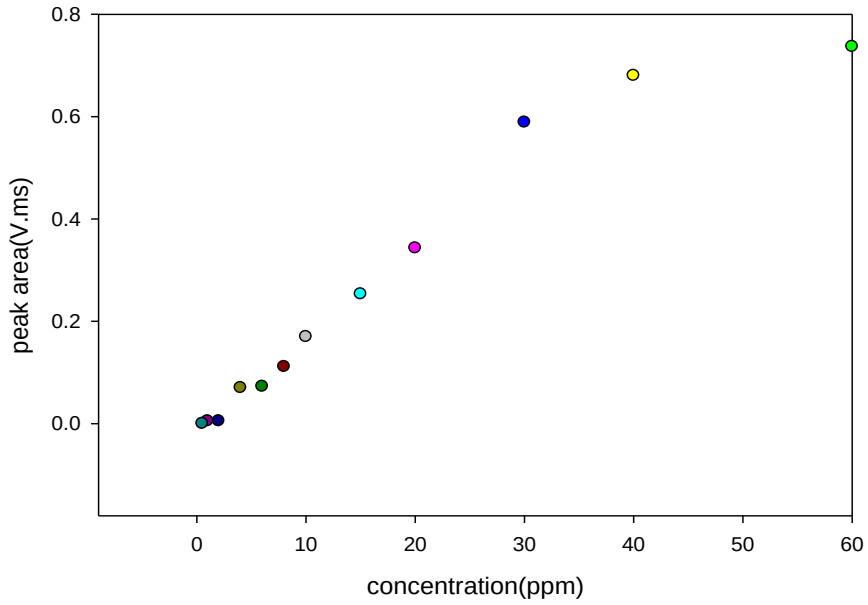


Figure (6) Phosalone calibration curve at 0.5-100 ppm concentrations

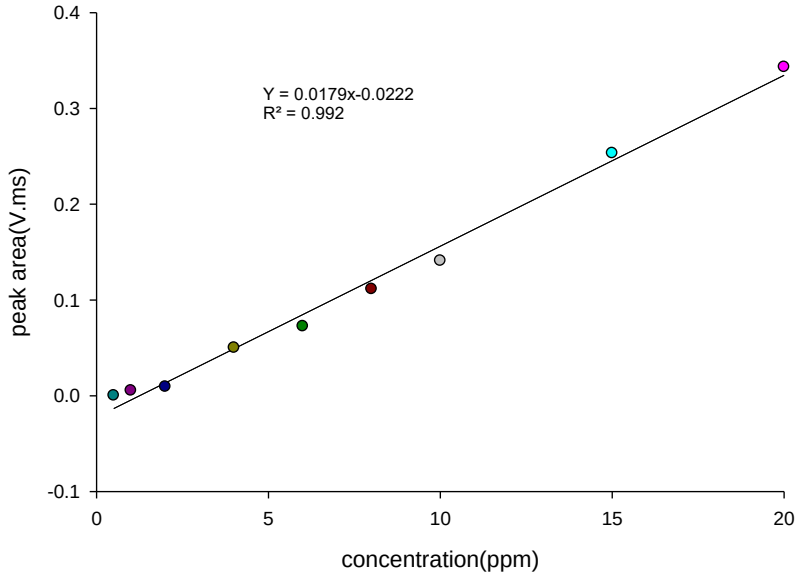


Figure (6) The linear range of Phosalone calibration curve

5. detection limit of ion mobility spectrometer (LOD)

The minimum concentration that a method can detect with a certain degree of confidence (Goscinny, Séverine, et al. 2015). In general, the detection limit is the concentration in which the device signal has a significant difference from the background signal. To calculate the detection limit, equation (1) is used (Ali Dini, Ali Alizadeh Spring 2018. .), where Sb is the standard deviation for the control sample and m is the slope of the calibration curve. To calculate the detection limit, the sample was injected into the

device 12 times and the standard deviation was calculated. The detection limit for Phosalone in optimal conditions was 1.412 ppm.

$$LOD = 3/3(\frac{0/00621}{0/0222}) = 1/412$$

6- limit of quantification (LOQ)

The limit of quantification of a method is the smallest sample concentration that can be determined with an acceptable uncertainty. In fact, it is the limit in which the difference between two different values can be reasonably recognized. The reduction limit is obtained from relation (2). In equation (2), Sb is the standard deviation of the control sample, m is the calibration slope, and LOQ is the limit of determination. The detection limit is 3 times the standard deviation of the control sample and the quantification limit is 10 times the standard deviation of the control sample.

The minimum concentration that the analytical method can determine and measure with a certain certainty is calculated from the following equation and its value is obtained.

$$LOQ = \frac{10S_b}{m} \qquad (۲)$$

$$LOQ = 10(\frac{0/00621}{0/0132}) = 4/731$$

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