Abstract
Negative ion spectrum for Endosulfan (Thiodan, 6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano 2,4,3-benzodioxathiepin-3-oxide) has been studied in air at ambient pressure using ion mobility spectrometry method. The detection limit and dynamic range of this compound, is $4.0 \times 10^{-10}$ g and $10^2$, respectively. Furthermore, in this study, the influence of cell temperature and sample amount on the ion mobility spectrum of Endosulfan was investigated.

Key Words: Endosulfan; Ion mobility spectrometry

Introduction
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 world-wide scale [1]. Therefore rapid, simple and sensitive field methods are required to check the presence of these compounds.

Organochlorinated compounds (OCCs) are the major group of the pesticides. So far, traditional methods such as: gas chromatography (GC) [2], high performance liquid chromatography (HPLC) and GC coupled with mass spectrometry (GC-MS) [3] have been used for analysis of these compounds. However these methods are known to be expensive and quite laborious. Ion mobility spectrometry (IMS) has been proven to be one of the best methods for the detection of trace level of OCCs.

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. 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. Early instruments for IMS exhibited picogram detection limits without sample preconcentration and generated strong interest in the technique. Organochlorinated compounds have high electron affinity and therefore readily produce negative ions in the reaction region of the ion mobility spectrometer, even in the presence of several other constituents present in ambient air [4].

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 [5]. Typically, the ion source has been 10 mCi of $^{63}$Ni electroplated on a foil, although other sources such as corona discharge [6], photo-ionization, and electrospray [7] ionization have been demonstrated. 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 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. 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 APCI
reactions between the sample vapors and a reservoir of charge called the reactant ions. Pesticides possess relatively high electron and proton affinity groups in the gas phase and are best observed as negative and positive ions [4,5]. The reactant ions in negative polarity are thermalized electrons in nitrogen and are hydrated O₂ or CO₂ with air. In order to enhance sensitivity and to remove background interferences, reagent gases may be used to create alternate reactant ions that provide additional selectivity in response.

**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 whit 17 cm long was made from 15 stainless steel rings whit 2.8 cm inner diameter that separated from each other by thin PTFE sheets. Schematic diagram of the apparatus is shown in Fig. 1. A 12 mCi-63Ni foil is used as an ionization source in this cell. The rings are 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 steel cap is 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 is used for introducing of sample vapor to ionization source. The gas was filtered with a 13X 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 spectrum of the compound are shown in Table 1.

![Fig. 1. Schematic diagram of ion mobility spectrometer instrument](image-url)
2.2. Chemicals and solutions

The chemical solvent used in this work is acetone that was obtained from Merck. Commercial-grade Endosulfan was obtained from Plant Protection Organization (Tehran). Stock standard solution (50 ppm) of this compound was prepared in acetone and then working solutions were made by successive dilution of the stock solution.

Results and discussion

3.1. Quantitative analysis

The ion mobility spectrum of Endosulfan is shown in the Fig. 2. The spectrum shows two peaks for Endosulfan and negative ion peak corresponding to reactant ions. In this work, acetone is used as a reagent gas to create alternate reactant ions that provide additional selectivity in response. The area of two peaks of Endosulfan is corresponding to amount of compound that is transfered to IMS cell by carrier gas. 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 (from the injection time until the sample peaks disappear) the relative peak area is changed. The 3D plot of the mobility spectra obtained by exposure to varying concentrations of Endosulfan is shown in Fig. 3. The sum of the peak areas (total) against the acquisition time is also shown in the fig. 4. The integration of this plot was considered as the response.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of drift tube</td>
<td>8.0 cm</td>
</tr>
<tr>
<td>Applied field</td>
<td>250 V cm</td>
</tr>
<tr>
<td>Drift gas (air)</td>
<td>600 ml/min</td>
</tr>
<tr>
<td>Carrier gas (air)</td>
<td>350 ml/min</td>
</tr>
<tr>
<td>Drift temperature</td>
<td>150 ºC</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>140 ºC</td>
</tr>
<tr>
<td>Pressure</td>
<td>630 torr</td>
</tr>
<tr>
<td>Gate widths</td>
<td>200μs</td>
</tr>
</tbody>
</table>

Fig. 2. The ion mobility spectrum of Endosulfan
Fig. 3. A watershed 3D representation of the mobility spectra obtained by exposure to varying concentrations of Endosulfan.

Fig. 4. The sum of the peak areas (total) against the acquisition time.
The response against amount of the compound was evaluated by plotting the calibration curve (Fig. 5). This Figure shows that the minimum amount of detection is 5 ng and the linear range is $5\times10^{-9}$-$5\times10^{-8}$ g for Endosulfan. Detection limit of this method for determination of Endosulfan is calculated by the equation of E1 that $S_B$ and $m$ are the standard deviation of blank and the slope of the calibration curve respectively.

$$LOD = \frac{3S_B}{m}$$  \hspace{1cm} (E1 equation)

The LOD calculated for this compound is $4.0\times10^{-10}$ g. The detection limit obtained is lower than that of the other methods for determination of Endosulfan. Furthermore this method has the very low response time (~5 sec) and the portable IMS can be achieved easily. Therefore a portable IMS can be made for detection and identification of trace residue pesticides in foods.

![Figure 5. Plot of IMS response against the amount of Endosulfan. The plot shown as onset of this figure shows the linear section of the calibration curve.](image)

3.2. Cell temperature and sample amount effect on spectrum

In this work, the influence of IMS cell temperature and sample amount on the Endosulfan spectrum was also investigated. The results of these studies are shown in Fig. 6.
and 7 respectively. According to these Figures, when the cell temperature or the sample amount are increased, no variation appears at the number of peaks.

**Conclusions**

IMS is a separation technique that affords qualitative information associated with the average cross-sectional area of ions. When interfaced with a mass spectrometer, data can be collected which gives additional qualitative information (i.e., mass information). IMS has been successfully coupled to quadrupole, time-of-flight and Fourier-transform ion cyclotron resonance mass spectrometry using radioactive $^{63}$Ni, electrospray, laser, and matrix-assisted laser desorption ionization sources. Applications have been reported for the analysis of illicit drugs, explosives, chemical warfare degradation products, biomolecules, and combinatorial chemistry samples. Ion mobility has the very low response time (~5 sec) and detection limit (pg). Furthermore, the portable IMS can be achieved easily. 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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**References**


