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Negative corona discharge-ion mobility spectrometry as a detection system for low density extraction solvent-based dispersive liquid–liquid microextraction

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ABSTRACT

This paper deals with a method based on negative corona discharge ionization ion mobility spectrometry (NCD-IMS) for the analysis of ethion (as an organophosphorus pesticide). The negative ions such as O_2^- and NO_x^- were eliminated from the background spectrum to increase the instrument sensitivity. The method was used to specify the sample extracted via dispersive liquid–liquid microextraction (DLLME) based on low density extraction solvent. The ion mobility spectrum of ethion in the negative mode and the reduced mobility value for its ion peak are firstly reported and compared with those of the positive mode. In order to combine the low density solvent DLLME directly with NCD-IMS, cyclohexane was selected as the extraction solvent, helping us to have a direct injection up to 20 μL solution, without any signal interference. The method was exhaustively validated in terms of sensitivity, enrichment factor, relative recovery, and repeatability. The linear dynamic range of 0.2–100.0 μg L^{-1}, detection limit of 0.075 μg L^{-1}, and the relative standard deviation (RSD) of about 5% were obtained for the analysis of ethion through this method. The average recoveries were calculated about 68% and 92% for the grape juice and underground water, respectively. Finally, some real samples were analyzed and the feasibility of the proposed method was successfully verified by the efficient extraction of the analyte using DLLME before the analysis by NCD-IMS.

1. Introduction

Organophosphorus pesticides (opps) are widely used as insecticides and acaricides for increasing agricultural productivity. These compounds are harmful to human health because they act on the central nervous system. As the opps compounds have long half-lives, their residues can remain in surface water, groundwater, soil and agricultural products [1]. Therefore, development of an analytical method with high accuracy and sensitivity for the determination of these compounds' residues is necessary. In this regard, various preparation methods such as liquid–liquid extraction (LLE) [2], solid-phase extraction (SPE) [3], solid-phase microextraction (SPME) [4] and single-drop microextraction (SDME) [5] have been utilized for the analysis of opps pesticides in various matrices. In LLE method, in addition to several tedious steps of preparation and extraction, a large amount of hazardous and toxic organic solvents has to be used. These disadvantages make the environment pollution require a long time to achieve the equilibrium, and cause loss of sample at each step [6]. In SPE method, though the time and solvent volume needed are comparatively less than in LLE method, the SPE method, nevertheless, requires toxic organic solvents for the elution step [7]. The next method, namely, SPME method suffers from a variety of drawbacks including high cost, short lifetime and fragile extractive fibers, and sample carry–over effect [8]. Also, the SDME methods impose some limitations such as the need for fast stirring speed, instability of hanging drop, and possibility of dissolving of the drop during the extraction process [9]. To overcome some of these problems, dispersive liquid–liquid microextraction (DLLME) method was firstly developed by Rezaee et al. in 2006 [10]. The major advantages of this method are low time and cost, simplicity of operation, high recovery, high enrichment factor (EF), and low consumption of organic solvents [11]. These advantages are luring the scientists into using this method for the extraction and preconcentration of a wide variety of pesticides from different environmental and foodstuff samples. In this method, a cloudy solution is formed when an appropriate mixture of extraction and dispersive solvent is injected into an aqueous sample. This cloudy solution results from tiny droplets of extraction solvent dispersed into the aqueous sample. In order to take out the analyte from aqueous phase with a high potential, the extraction solvent must be soluble

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in the dispersive solvent while having a very low solubility in water. After centrifuging, tiny droplets of extraction solvent containing analyte can be collected in lower or upper aqueous phase, based on the density, and then separated from the aqueous phase. Only some solvents which have a higher density than water can form a cloudy solution in DLLME technique [12]. Typically, in this case, chlorinated solvents such as chloroform, tetrachloromethane, chlorobenzene and tetrachloroethane are used as the extraction solvents. These solvents are very toxic and hazardous to humans and environment. In addition, chlorinated solvents have a very high electron affinity and therefore produce a strong signal using analytical apparatus in the negative mode such as gas chromatography-electron capture detector (GC-ECD) or mass spectrometry (MS). In fact, as the solvent signal may overlap with some analyte peaks, the DLLME–GC-ECD technique cannot be used to extract and measure the opps pesticides. To overcome these problems, Farajzadeh et al. [13] used some solvents lighter than water as the extraction solvent, for the first time. In DLLME based on the low density extraction solvents, all the treatment steps except the steps after centrifuging are the same as those in the technique with solvents heavier than water. Unlike the heavy solvents, low density extraction solvent droplets were delivered on the surface of the aqueous phase. For collection of the extracted phase, some special extraction tubes were designed and developed for DLLME procedure [12–14].

In DLLME technique, the collected organic phase can be monitored using several methods such as GC with different detectors [13–15] or high performance liquid chromatography (HPLC) with various detectors [16,17]. However, these methods are very laborious and require a long run time for separation in a column [18]. In addition, HPLC methods require expensive solvents in the elution step. Very recently [19], we have described the feasibility of corona discharge ion mobility spectrometry (CD-IMS) in the positive mode as a detection system for DLLME extraction procedure. Based on the obtained results, it was concluded that IMS could be used as a very fast and sensitive method with no vacuum required for the analysis of analytes extracted by DLLME. However, in some cases it is necessary to develop the negative corona discharge ion mobility spectrometry (NCD-IMS) for the analysis of some chemical compounds with more sensitivity compared with positive the mode. In this regard, some problems such as limitations on selection of extraction solvent must be considered.

Considering the discussions above, the objective of this work is to develop the application of CD-IMS in the negative mode as a detection system for DLLME method based on low-density extraction solvent. The ethion compound (as anorganophosphorus pesticide) was extracted by DLLME procedure and the collected phase was directly injected into the NCD-IMS. Some parameters affecting the extraction efficiency such as type and volume of extraction solvent, type and volume of dispersive solvent, salt addition and pH effect were studied. The proposed method was applied to determine ethion residue in the grape juice and groundwater samples.

2. Experimental section

2.1. Instrumentation

The corona discharge ionization ion mobility spectrometer (CD-IMS) used for this research was designed and constructed at Isfahan University of Technology, described in detail previously [19]. In this work, however, the design of the ionization source was changed and a novel design of point-in-cylinder geometry was used to establish the corona discharge without interferences of negative ions such as NO_X^-. The details of this newly designed CD-IMS in negative mode have been presented in an Iranian patent [20]. Table 1 summarizes the negative CD-IMS operating conditions under which the mobility spectra were taken.

Table 1
Typical operating conditions of NCD-IMS during the experimental runs.

Operating parameters	Setting
Needle voltage	−2.7 kV
Target electrode voltage	−8.0 kV
Drift field	400 V cm^{-1}
Temperature of injector	200 °C
Temperature of cell	150 °C
Drift gas flow (N_2, 99.999%)	800 mL min^{-1}
Carrier gas flow (N_2, 99.999%)	400 mL min^{-1}
Drift tube length	11 cm
Shutter grid pulse	0.3 ms
Number of IMS averages	25
Number of points per ion mobility spectrum	500

2.2. Standard solutions and reagents

Ethion (99% purity) was obtained from Accustandard Company, USA. All the reagents used in this study such as cyclohexane, toluene, n-hexane, methanol, acetone and acetonitrile were HPLC grade prepared from Merck Company, Germany. The stock standard solutions were prepared in methanol with the concentration of 1000 mg L^{-1}. The standard working solutions with required concentrations were daily prepared by dilution of the stock solution using deionized water.

2.3. Sample preparation

Prior to carrying out the extraction using DLLME method, some sample pretreatment steps must be accomplished due to the solid matrix of sample grape. In this work, the sample was washed with water to remove the surface contaminants. Afterward, it was homogenized by a blender and then 1.000 g of the homogenized sample was accurately weighed and transferred into a 10-mL test tube. 100 μL of aqueous standard solution of ethion (1000 μg L^{-1}) was spiked to the sample and was diluted with 9 mL deionized water. Before DLLME procedure, the pesticide in the matrix was spread out from sample by heated water. For doing that, the test tube was heated at 70 °C for 60 min in steam bath. Coagulation of fibers could occur in the sample matrix during the warming of aqueous solution, increasing the extraction efficiency. The test tube was centrifuged at 3000 rpm for 15 min, helping us to separate fibers and other insoluble solid particles. Finally, 5 mL of supernatant solution was transferred into the extraction vessel.

2.4. DLLME procedure

DLLME procedure was carried out for 5 mL ethion aqueous solution transferred into the extraction vessel designed for low density extraction solvent. The extraction vessel used in this work was designed previously by Farajzadeh et. al [13]. The bottom of the extraction vessel was closed by a septum. 0.5 mL methanol (as dispersive solvent) containing 40 μL cyclohexane (as extraction solvent) was rapidly injected into the solution using 2-mL syringe, resulting a cloudy solution. The cloudy solution was centrifuged for 5 min at 3000 rpm for separating the organic phase from aqueous phase. In this DLLME procedure, organic phase containing the extracted analyte was collected on the upper aqueous phase due to the lower density of cyclohexane. In the next step, 2 mL deionized water was gently injected into the extraction vessel through the septum, helping us to transfer the organic phase into the narrow neck of the extraction vessel. This results in simple collection of the organic phase by a 25-μL microsyringe. Finally,

5 μL of collected solution was directly injected into the NCD-IMS through the injection port designed previously [19].

3. Results and discussion

3.1. Ion mobility spectra

The background ion mobility spectrum of negative corona discharge ion mobility spectrometry (NCD-IMS) is shown in Fig. 1.

According to this figure, the spectrum shows only one peak which appears in the minimum drift time corresponding to electrons. In fact, with the newly designed NCD-IMS used in this work [20], the diffusion of the atmospheric oxygen into the corona discharge region was prevented. This can preclude the production of negative ions such as O_2^- and NO_x^- in ionization region, eliminating their signals from the background spectrum. Existence of these ions in ionization source causes significant administrative troubles. First, the NO_X cluster ions have very high electron affinities (~3.9 eV) and therefore, they can essentially quench the formation of product ions for even halogenated compounds [21]. Second, in the presence of NO_X^-, O_2^-, and other negative ions in ionization source [22] it is impossible to analyze these gases themselves in a sample. Third, these ions occupy one part of the spectrum and therefore their signals may overlap other sample peaks. Finally, these negative ions can join the sample molecules and as a result, various clusters of analytes would be inevitable, making it difficult to interpret more complex ion mobility spectra. Thus until recently, continuous corona discharge ionization source has not been a suitable candidate for the replacement of ^{63}Ni in negative ionization mode and therefore, the broad-scale use of the negative continuous corona discharge source for IMS has been stalled. Consequently in this novel design, the sensitivity was significantly increased due to enhancing the electron current obtained during the corona process. This causes a very high signal to noise ratio that can be easily observed in the plot shown at the inset of Fig. 1.

3.2. Ion mobility spectrum of ethion

Fig. 2 shows the spectra of ethion compound in the negative and positive modes compared with those of backgrounds. To obtain these spectra, ethion solution in methanol was directly injected into the injection port in both of the IMS modes. It must be noted that for an acceptable comparison of drift time, all the operation conditions such as cell temperature (150 °C) and voltage of drift region (8.00 kV) must be constant in both modes of apparatus.

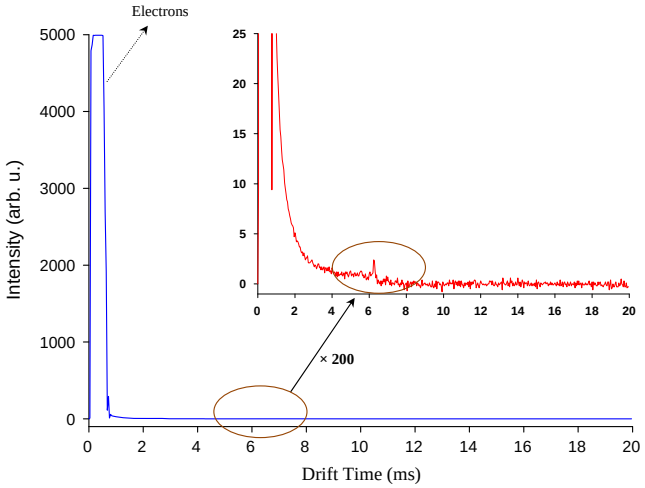

Fig. 1. The background ion mobility spectrum of negative corona discharge IMS. The spectrum illustrates very high signal to noise ratio without any considerable interference of negative ions (e.g. NO_x^-, O_2^-, etc).

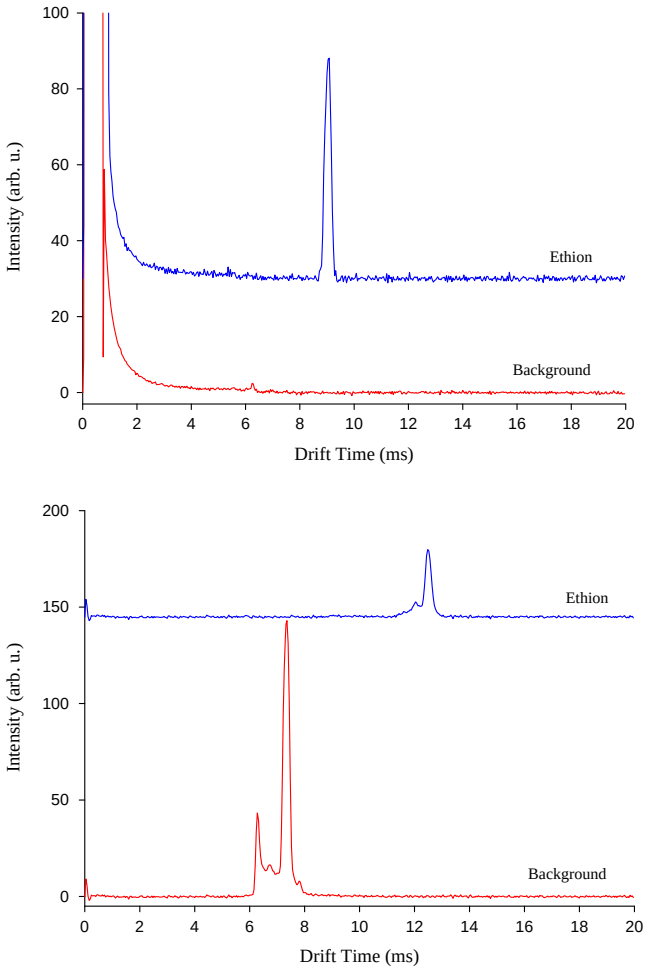

Fig. 2. The ion mobility spectra of ethion and background obtained by CD-IMS in negative (top) and positive (bottom) modes.

As can be observed, ethion in the positive and negative modes was detectable; however, their drift times and intensity values were dramatically different. The spectra show one ion peak at drift times of 12.52 and 8.56 ms in the positive and negative modes, respectively. In order to calculate the reduced mobility values of ethion in the positive and negative modes, nicotinamide (K_o=1.85 $cm^2\,v^{-1}\,s^{-1}$) and trinitrotoluene (K_o=1.50 $cm^2\,v^{-1}\,s^{-1}$) were used as standard compounds, respectively. The reduced mobility values of 1.11 and 1.58 $cm^2\,v^{-1}\,s^{-1}$ were calculated for ethion ion clusters in the positive and negative mode, respectively. The K_o value of ethion in the positive mode is very close to that reported by Jafari (1.09 $cm^2\,v^{-1}\,s^{-1}$) using ESI-IMS [23]. In the negative mode, however, there is no any reported value for the reduced mobility, making it impossible to compare the obtained K_o value in this work. In fact, to assign the ionic species more definitely in the positive and negative modes, it is necessary to couple MS to IMS. However, the results reported previously on mass spectrometry studies of ethion may be helpful for this assignment. A formation mechanism for OPPs positive ions using positive atmospheric pressure chemical ionization MS was suggested by Portolés et al. [24]. Based on their results, OPPs can produce $[MH]^+$ ions via proton transfer reaction in corona discharge ionization source. In addition, the molecular ion of $[MH]^+$ was detected for ethion using the electrospray ionization MS in the positive mode [25]. Electrospray is known as a soft ionization source through which fragmentation of analyte molecules does not usually

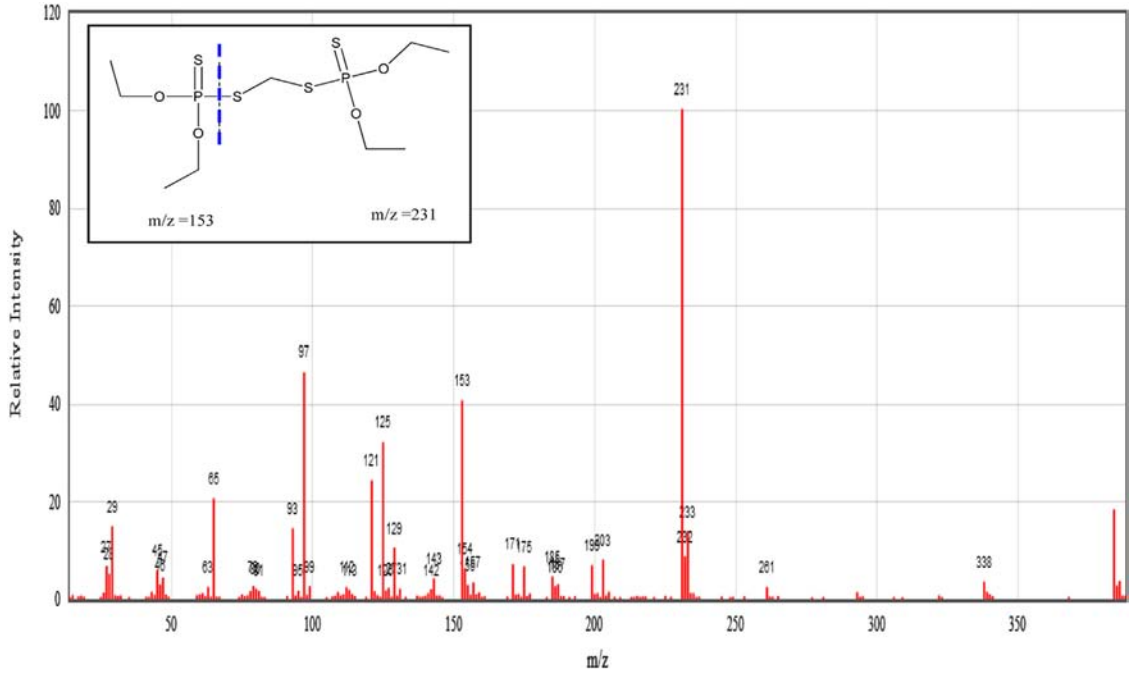

Fig. 3. The electron impact-mass spectrum reported in NIST library plus chemical structure of ethion.

occur. Considering the discussion above, the ethion peak observed in the positive mode of IMS may be due to the formation of $[MH]^+$ ion cluster.

On the other hand, the ion mobility spectrum in the negative mode (Fig. 2) shows a lighter ion cluster originated from ethion. The mass spectra of ethion compound obtained from NIST library with electron impact ionization source are shown in Fig. 3 [26]. This figure displays some fragments of the ethion created in ionization region of MS. The ion corresponding to $m/z=231$ shows most intensity. An explanation is that the ethion molecule may be broken down via energetic electron impact in the ionization region, as shown at the inset of Fig. 3. Lambropoulou et al. [27] observed the base ion peak with $m/z=231$ assigned to structure of $(CH_2S_2–(C_2H_5O)_2PS)$. In this work, the electron impact as the ionization mechanism in negative corona discharge helps us to assign the negative ion molecule of ethion to $(CH_2S_2–(C_2H_5O)_2PS)$. As a result, unlike the positive mode, ethion fragmentation can occur in the negative mode, producing an ion species which has a lower mobility than that observed in the positive ion.

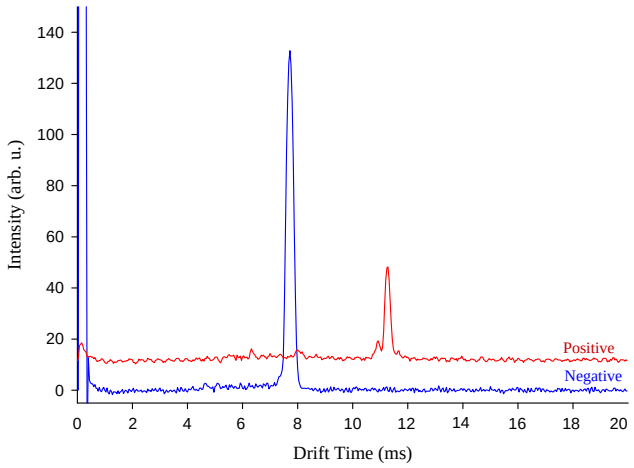

Fig. 4. The ion mobility spectra obtained for ethion solution (10.0 mg L^{-1}) using CD-IMS in positive and negative modes. The quantitative results indicate the intensity in negative mode is about 25 times greater than that of positive mode.

3.3. Comparison of sensitivity in positive and negative modes

In order to compare the sensitivity of negative and positive CD-IMS for ethion, 5 μL methanol solution (10.0 mg L^{-1}) was injected into the instrument, in both modes. It must be noted that all the operating parameters affecting sensitivity were the same in both modes. The obtained results are shown in Fig. 4, demonstrating an ion peak with more intensity in the negative mode than that obtained in the positive mode. This indicates a significant higher sensitivity achieved when ethion is analyzed in negative mode.

As illustrated in this figure, the reactant ions peaks $(H^+(H_2O)_n)$ were completely eliminated from the spectrum, revealing the saturation of the signal in the positive mode. In other words, the limited reactant ions in the positive mode were totally consumed for ionization of ethion molecules. On the other hand, as shown in Fig. 4, negative ion mobility spectrum of the compound shows an ion peak with a considerable intensity corresponding to electrons, in addition to analyte signal. This proves that no limitation is observed in ionization reaction of analyte when the negative mode is selected for analysis. For more investigation of the sensitivity, various analyte solutions were prepared and the IMS responses were obtained after the injection of 5 μL of the analyte solutions in both modes. The limits of quantification were determined to be 20.0 and 500.0 μg L^{-1} in the negative and positive modes, respectively. To date, IMS in the positive mode has been used for the analysis of several organophosphorus compounds [19,23,28,29]. In this work, however, the results obtained by negative corona discharge IMS reveal the sensitivity about 25 times greater than that of the positive mode for the analysis of ethion. Other analytical parameters such as dynamic range and relative standard deviation were calculated in only the negative mode to be 20–8000 μg L^{-1} and 6% (for 500 μg L^{-1}), respectively. Consequently, the negative mode of CD-IMS was selected for analyzing the ethion extracted by DLLME technique.

3.4. Optimization of the experimental conditions of DLLME

In order to obtain high extraction efficiency, the effects of various parameters such as type of extraction and dispersive solvents and

their volumes, salt addition, and pH of solution were investigated. The peak area was calculated from the appearance to disappearance of the analyte signal and considered as the IMS response. All the experiments were repeated three times and the resulting average values are shown in tables and curves.

3.4.1. Type of extraction solvent

As discussed in the Section 1, it is not possible to use the chlorinated solvents in negative corona discharge ionization ion mobility spectroscopy. In fact, the halogenated compounds have a high electron affinity which competes with the analyte for electron capturing, thus diminishing the sensitivity of the method. This problem might occur so harshly that no signal can be observed even for the analyte with a high concentration. Therefore, an appropriate extraction solvent with minimum electron affinity must be selected in order to eliminate the additional ionic species in the negative ion mobility spectrum. On the other hand, maximum analyte must be extracted from the aqueous samples by the selected solvent, during the DLLME method. For the selection of the extraction solvent, 5 μL of various organic solvents such as cyclohexane, n-hexane, and toluene were directly injected into the injection port and the corresponding spectra were recorded (data not shown). The obtained results illustrate the interference signals with a much lower intensity relative to the signal of the chlorinated solvents. In addition, the best solvent selectivity was evaluated for the extraction of a 5 mL aqueous sample with (100 μg L^{-1}). In this regard, 1 mL methanol as the dispersive solvent containing different volumes of extraction solvents was used to achieve a similar volume of the organic phase collected in narrow neck of the extraction vessel. To achieve about 20 μL of the extracted phase, 50, 40, and 40 μL of toluene, cyclohexane, and n-hexane are to be used, respectively. The CD-IMS responses were calculated to be 25786 ± 774, 25124 ± 1256, and 42249 ± 1267, obtained after injection of n-hexane, toluene, and cyclohexane, respectively. According to these results, the extraction efficiency of cyclohexane is higher than that of the other two solvents. Also, according to the reported data by Farajzadeh et al. [13] cyclohexane has a more extraction efficiency for the analysis of ethion in water samples. Hence, cyclohexane was selected as an extraction solvent for the subsequent experiments in this work.

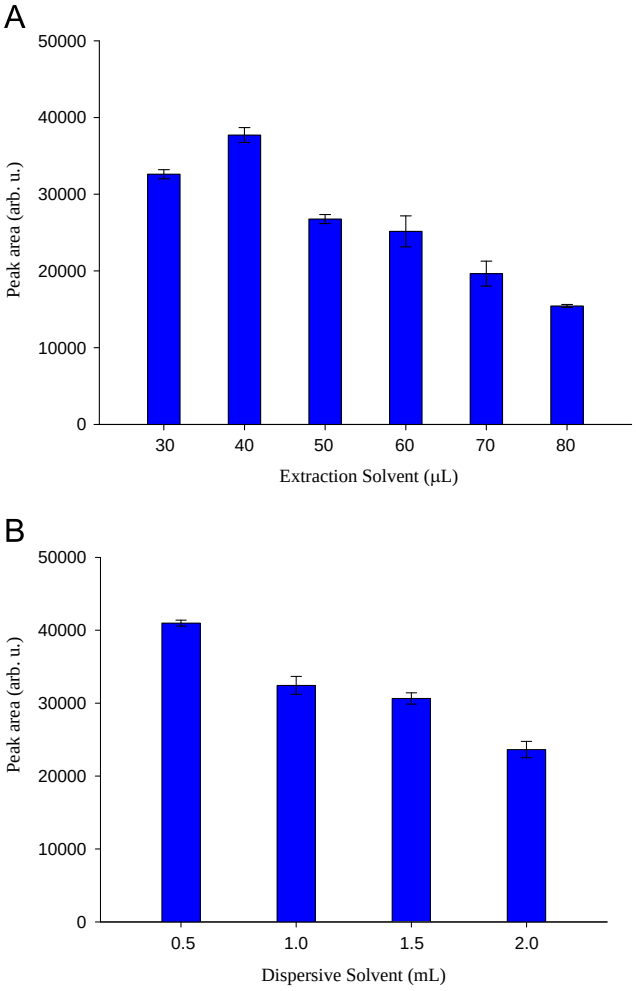

Fig. 5. The volume effect of, (A) cyclohexane as the extraction solvent and (B) methanol as dispersive solvent on the efficiency of extraction.

3.4.2. Type of dispersive solvent

The miscibility in the aqueous phase (sample solution) and organic phase (extraction phase) is the main criterion for the selection of dispersive solvent. Also, this solvent must be able to disperse the extraction solvent as very fine droplets in the aqueous phase. This can increase the contact area between organic and aqueous phases, resulting in higher extraction efficiency. In this study, methanol, acetone, and acetonitrile were studied as the dispersive solvents. The extraction was carried out from 5 mL ethion standard solution (100 μg L^{-1}) using 40 μL cyclohexane plus 1 mL of each dispersive solvent. According to the obtained results (data not shown), the highest extraction efficiency is obtained when the methanol is used as the dispersive solvent. As a result, methanol was selected as the dispersive solvent for more experiments.

3.4.3. Effect of volumes of extraction and dispersive solvents

To evaluate the volume effect of the extraction solvent on the extraction efficiency, 1 mL methanol containing different volumes of cyclohexane (30, 40, 50, 60, 70 and 80 μL) was used for extraction of ethion existing in 5 mL aqueous standard solution (100 μg L^{-1}). Based on the results shown in Fig. 5A, the IMS response was increased from 30 to 40 μL and then decreased when the volume of cyclohexane was increased to 80 μL. The lower intensity obtained in 30 μL may be due to dissolving a larger volume of the extraction solvent in aqueous phase, resulting in formation of lower droplet numbers. After 40 μL, a decrease was however observed because of the analyte dilution in a larger volume of the upper phase (extracted phase). Consequently, 40 μL of cyclohexane was selected as the optimum volume of extraction solvent in subsequent experiments.

To obtain optimum dispersive solvent volume, all the experimental conditions were fixed at their optimum values except the volume of methanol which was varied from 0.5 to 2 mL.The results (Fig. 5B) showed that the peak area of analyte is decreased by increasing the methanol volume due to ethion solubility enhancement in the aqueous phase. It must be noted in the volumes less than 0.5 mL, no cloudy solution was observed well, thereby extraction could not be carried out desirably. So, for the best extraction efficiency, 0.5 mL methanol was selected as the optimum volume of dispersive solvent.

3.4.4. Salt addition effect

To investigate the effect of salt addition, the extraction was carried out from 5 mL of aqueous solution of ethion with the concentration of 100 μg L^{-1} containing 0, 0.05, 0.10, 0.15 and 0.20 g mL^{-1} sodium chloride. Other experimental conditions were kept constant in their optimum values. The results shown in Fig. 6A indicate that by increasing the salt concentration the ionic strength of the solution is changed, thus diminishing the extraction recovery. An explanation is that decreasing the extraction solvent solubility in the aqueous phase increases the volume of the

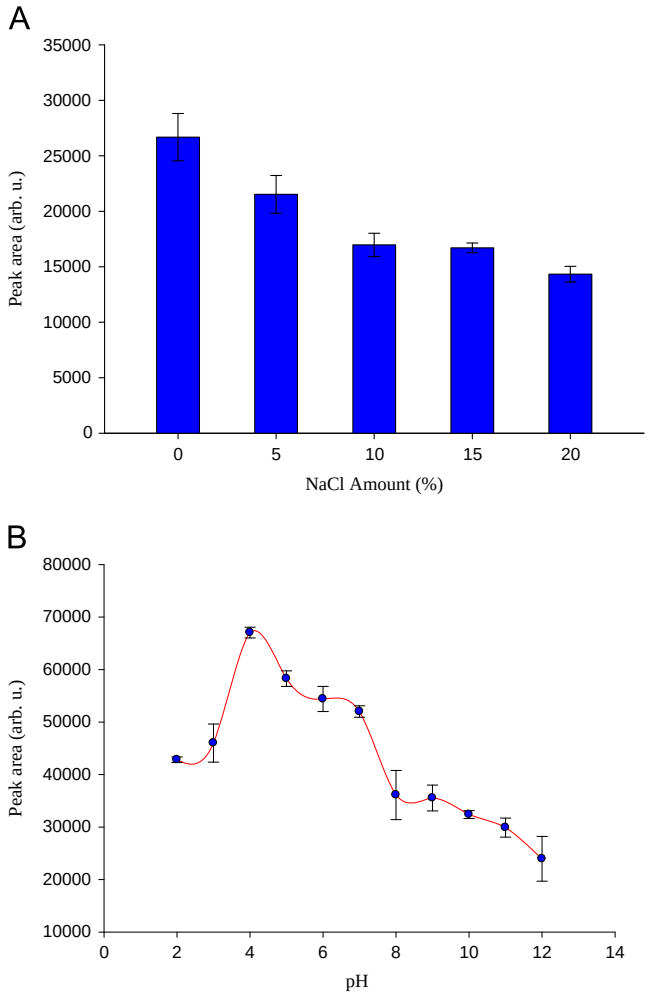

Fig. 6. The effects of, (A) NaCl amount and (B) solution pH on the extraction efficiency.

collected extraction solvent. Hence, further extractions were done without the addition of any salt.

3.4.5. *Effect of pH*

The effect of pH on the extraction efficiency was studied within the pH range of 2–12, the obtained results of which are illustrated in Fig. 6B. As this figure shows, better extraction efficiencies could be obtained at pH 4. In the solution with pH lower than 4, ethion can be protonated, decreasing the IMS signal for the extracted samples. On the other hand, if pH is increased the ethion molecules are hydrolyzed and as a result signal diminishing is observed at pH higher than 4. In other words, according to our obtained results protonation and hydrolysis of ethion is minimum at pH 4, and the analyte is in molecular form. This is in good agreement with the results reported by Dierberg and Pfeuffer [30] and Barabas [31]. Hence, pH 4 was considered most favorable for extraction in next experiments.

3.5. *Method validation*

In order to examine analytical characteristics used in this study, figures of merit including repeatability, dynamic range, detection limit, and enrichment factor were calculated under optimum conditions. In this regard, various standard solutions of ethion in water were prepared and the extraction process was accomplished under the optimum conditions, as mentioned in Section 2.4. Fig. 7 shows the ion mobility spectra obtained after the injection of 10 μL pure cyclohexane and 5 μL cyclohexane containing analyte extracted from 10 μg L^{-1} aqueous solution.

As can be observed, the ion mobility spectrum of pure cyclohexane shows no considerable ion peak, indicating that no interference can originate from extraction solvent. After direct injection into the negative CD-IMS, the peak area was calculated and considered as the IMS response for each concentration. A favorable

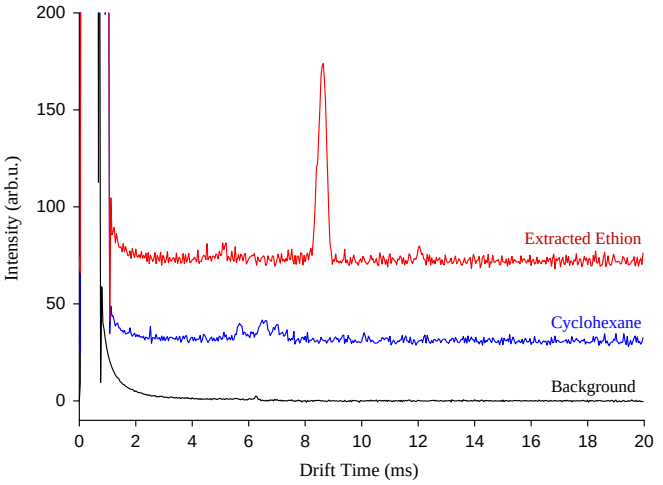

Fig. 7. The ion mobility spectra of background, pure cyclohexane (as extraction solvent), and ethion extracted from water sample (10 μg L^{-1}).

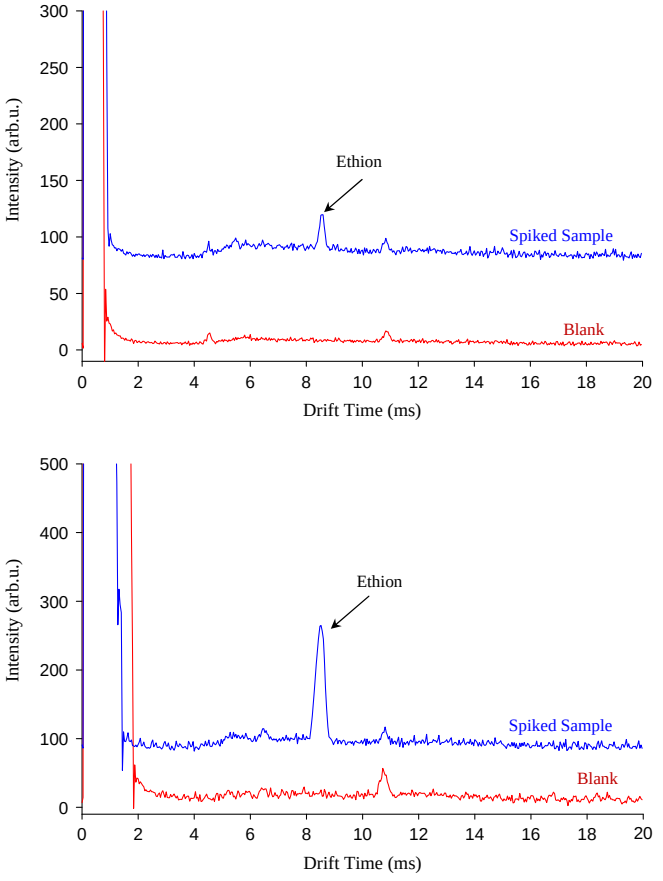

Fig. 8. The ion mobility spectra of ethion extracted from grape juice (top) and underground water (bottom) samples, compared with those obtained for their blanks.

linear range was obtained for ethion from 0.2 to 100.0 μg L^{-1} with a determination coefficient of 0.997. With optimal conditions at hand, the average value of intra-day relative standard deviation was obtained to be less (about 5%) for triplicate extraction (for 2.0, 10.0, 50.0 μg L^{-1} solutions). In order to calculate the inter-day relative standard deviation, extraction was also carried out from aqueous solution of ethion with a concentration of 10 μg L^{-1} on three consecutive days (three repeated measurements on each day) and the accepted value of 7% was calculated. By standard definition $S/N=3$, the detection limit of this method was calculated 0.075 μg L^{-1}. In this study, enrichment factor was calculated as the ratio of the final analyte concentration in organic phase to the initial concentration in the aqueous solution. This was accomplished for triplicate extractions of analyte from water samples spiked with 20 μg L^{-1} analyte. The EF value obtained was 60, revealing an acceptable enrichment factor.

3.6. Real sample analysis

In order to investigate the capability of the proposed method for analyzing real samples, underground water and grape juice were analyzed under the optimum conditions. The residual analyte was extracted from samples before DLLME extraction step based on the method described in Section 2.3. The ion mobility spectra of extracted samples compared with those of corresponding blanks are shown in Fig. 8.

As can be observed in blank spectra, there is no ion peak with a drift time of 8.56 ms (for ethion), indicating that no significant analyte was extracted during the DLLME method. This observation also reveals that no serious matrix interference (with the same drift time) was extracted along the analyte. However, for more confidence, multiple addition methods were carried out to overcome any probable matrix interference. In this regard, the underground water and grape samples were spiked by standard solutions at different concentrations (20, 50, 100, 200, 500, and 1000 μg L^{-1}) and then the ethion was extracted. The relative recoveries as well as some figures of merit obtained in these experiments are summarized in Table 2. The results demonstrate the capability of DLLME-NCD-IMS for the analysis of ethion in real samples. In fact, the proposed method was established without any tedious sample pretreatment which is very effective and simple enough to be conveniently used by anyone familiar with IMS.

Table 2
Quantitative characteristics of the proposed method (DLLME–NCD-IMS) for the study of matrix effect in grape juice and ground water samples spiked with 20, 50, 100, 200, 500, and 1000 μg L^{-1} of ethion.

Sample type	Relative recovery %	Dynamic range (μg L^{-1})	LOD (μg L^{-1})	RSD[a] ($n=3$) %	EF	r^2
Standard solution	–	0.2–100	0.075	5	60	0.997
Grape sample	68	2.0–100	0.80	6	35	0.995
Groundwater sample	92	0.3–100	0.12	8	50	0.998

[a] Relative standard deviation obtained from solution with concentration of 20 μg L^{-1}.

3.7. Comparison between the proposed method and other methods

Table 3 shows the comparison of some analytical characteristics such as linear dynamic range, limit of detection, relative standard deviation, and recovery values obtained in the proposed method with those reported in some previous works. In most cases, an expensive and time consuming technique such as GC or HPLC has been used for separation of analyte from the matrices. Typically, an analysis by GC or HPLC takes about 15–30 min, whereas this time in CD-IMS is lower than 5 s. Therefore, the detection time in the proposed method was much shorter than that of the methods such as LC, and GC. Yet, the reliability was not lower than that of the other methods. It must also be said that some of the methods which have used MS as a detection system show sensitivity superior to that obtained in this work. But, MS technique is more expensive than IMS and also requires a vacuum system. According to the results, when the technique of DLLME based on low density solvents is combined with negative corona discharge-ion mobility spectrometry, it allows us to have a fast analysis with an admissible sensitivity, RSD, and recovery.

4. Conclusion

Ion mobility study of ethion pesticide was carried out in both positive and negative modes. The negative corona discharge ionization ion mobility spectrometry was selected as the detection system for dispersive liquid–liquid microextraction technique based on low density extraction solvent. Ethion was extracted from various real samples including grape juice and underground water, and then analyzed using the proposed method. The analysis time in this proposed method was much shorter compared with that required in some methods such as LC or GC. That is, both the extraction and

Table 3
Comparison of analytical parameters of the proposed method and other techniques for analysis of ethion in various samples.

Analytical method	Sample type	Linear dynamic range (μg L^{-1})	LOD (μg L^{-1})	RSD (%)	Recovery (%)	Reference
DLLME-GC-FID	Water	10–100000	4	5–8	84–91	[13]
DLLME-GC–MS	Water	0.01–1	0.003	7–9	84–92	[13]
SPE-DLLME-GC-FPD	Water	0.001–10	0.0002	4	95–102	[32]
RPLC[a]-GC-NPD	Olive oil	50–670	1.01	8.1	-	[33]
MASE[b]-GC–MS	Wine and apple juice	0.023–70	0.023	10	75–97	[34]
DLLME-GC–MS	Herbal medicines	0.5–1000	41×10^{-5}	4	72–112	[35]
DLLME-GC–MS	Fruits and vegetables	0.1–1000	11×10^{-5}	5.7	75–100	[35]
HS-SPME-GC-FTD	Water	0.05–1	0.015	13	89–118	[36]
DLLME-GC-FPD	Water	0.01–100	0.003	1.5–6	105–125	[37]
DLLME-HPLE	Apple, tomato, cucumber and water	10–4000	3	4.1	54.9–59.1	[38]
MSPD[c]-SPE-HPLC	Bovine tissue	1–10[d]	0.2[d]	3–10	95.5	[39]
DLLME-NCD-IMS	Water	0.2–100	0.075	5	68–92	Proposed method

[a] Reversed- phase liquid chromatography.
[b] Membrane-assisted solvent extraction.
[c] Matrix solid-phase dispersion.
[d] Data presented in μg g^{-1}.

detection of a sample took about 15 min. Furthermore, the reliability of this proposed method was equally acceptable. In addition to portability, IMS is much easier to use and is cost-effective compared to other methods, especially MS. The results obtained in this study demonstrate the benefits of rapidity, sensitivity, and convenience associated with DLLME-NCD-IMS used in real sample analysis.

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