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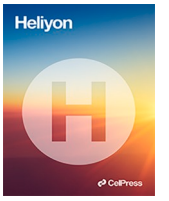

Research article

A configuration for cooling assisted organic solvent coated thin film microextraction after dispersive liquid-liquid microextraction method: A microextraction method for ultra-trace analyzing of volatile sample

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ABSTRACT

A combination of the dispersive liquid-liquid microextraction (DLLME) method based on the total vaporization procedure and cooling-assisted organic solvent-coated thin film microextraction (TFME) was applied for extracting chlorpyrifos (as the model compound). Based on the high thermal conductivity, a nickel foam thin film with the dimensions of 5.0 mm × 5.0 mm was used as a substrate for holding the organic solvent. Supporting thin film by organic solvent increases the thickness and contact area of the film relative to TFME or single drop microextraction (SDME) alone, resulting in a dramatic increase in the extraction efficiency. To protect the organic solvent and enhance the analyte distribution coefficient between the film and the vapor phase, a cooling system was applied. The proposed design was effective due to condensing the target analyte only on the uniform cooled thin film and not on the other regions in the extraction chamber. A corona discharge ionization source-ion mobility spectrometer was employed to identify the analyte. After optimizing the effective parameters, the limits of quantification (S/N = 10) and detection (S/N = 3) were calculated 0.1 and 0.03 μg L^{-1}, respectively, and the dynamic range was measured between 0.1 and 7.0 μg L^{-1}, with a determination coefficient of 0.9997. For three concentration levels of 0.1, 3.0, and 7.0 μg L^{-1}, the relative standard deviations (n = 3) as the repeatability index were to be 6 %, 5 %, and 4 % for intra-day and 9 %, 6 %, and 5 % for inter-day, respectively. The enrichment factor was also calculated to be 3630 for the analyte concentration of 1.0 μg L^{-1}. Well water, potato, and agricultural wastewater were analyzed as the real samples and the relative recovery values were measured between 92 % and 99 %. The accuracy of the proposed technique was validated by the European Standards EN 12393 method. In this approach, two steps of analyte extraction (DLLME and TFME) were used consecutively, resulting in better preconcentration and reduced matrix interference during cleaning-up.

1. Introduction

Matrix effects hamper the analysis of complex matrices directly [1]. To overcome these problems, researchers have introduced different solutions by applying the standard addition methods [2], various sample preparation techniques [3], and

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chromatographic-based methods [3–5]. Sedimentation, especially for biological samples or dilution, is one of the other ways to reduce the matrix effect. So far, different sample preparation methods, including solid-phase microextraction (SPME) [6], thin-film microextraction (TFME) [4], single-drop microextraction (SDME) [7], and dispersive liquid-liquid microextraction (DLLME) [5] have been used to mitigate the harmful effect of the matrix components on the analysis of analytes.

In 1990, Pawliszyn and Arthur [8] presented SPME as a cheap and simple method, without solvent elution of the extracted analyte. However, the important drawbacks of the SPME method are the negligible extraction phase, memory effect, the short lifetime of the fiber, mechanical instability of the fiber, release of the sorbent, high expensive of the commercial fibers, and high extraction time [9–11]. In 2003, a new SPME approach named TFME was introduced by Bruheim et al. [12]. Distribution of analyte between aqueous solution and a thin film, as the stationary phase, is the basis of this method and may be applied as the immersion or headspace techniques. High surface area to volume ratio, flexibility, mechanical stability of the thin film, and high lifetime are the main advantages of this method. Generally, the solid-based microextraction methods have some shortcomings including memory effects, complex and time-consuming steps for the synthesis of the adsorbent, and the high extraction time [11,13]. Owing to the adsorbent release during successive extractions, the sorbent could not be reused several times [1]. Accordingly, some solvent-based microextraction methods with considerable simplicity, rapidity, repeatability, and without memory effect were developed. In 2006, the DLLME method, as a novel design of the solvent-based microextraction method with high efficiency, was presented by Rezaee et al. [14]. In the DLLME method, firstly, a disperser and extraction solvents are mixed and injected into the analyte aqueous solution to create the cloudy solution. Then, centrifuging the cloudy solution and separating the collected solution to be detected by an instrumental analysis.

In 1970, the ion mobility spectrometry (IMS) technique was designed by Karasek and Cohen [15]. The simplicity, low cost, high sensitivity, and short response time are the benefits of this instrument as a detection system. The IMS instrument works based on the mobility of ion molecules in the gaseous phase and it has been applied for the detection of some compounds, including environmental pollutants, drugs, and pesticides [16]. In combination of DLLME with IMS, solvent interference may be produced, decreasing the precision, accuracy, and IMS signal of the target analyte [17,18]. To overcome this problem, the hyphenated method of DLLME-SPME was introduced by Jafari et al. [19]. Firstly, the DLLME method was performed to extract the analyte; then, all collected phase obtained by the extraction method was transferred into a vial for the SPME operation. The high preconcentration factor and no solvent interference are the major advantages of that method; however, releasing the SPME coating and being limited to the analysis of volatile compounds were remained. Also, in that work, the SPME fiber was warmed due to the total vaporization procedure; so the analyte distribution coefficient of the analyte between the fiber and vapor phase could be decreased sharply, deteriorating the extraction efficiency [20,21]. In a few reports [22–25], a generation of cooled SPME named cold fiber for extraction of the volatile compounds to increase the analyte distribution coefficient between the adsorbent and headspace sample was introduced. Recently, a distillation condenser, as a cooling zone, was applied to combine the headspace SPME with purge assisted [26]. The results revealed the approach of that method for more analysis of the volatile compounds with the lowest effect of the sample matrix. However, the main challenges are the condensation of analytes on the SPME fiber and other regions of the extraction setup and inapplicability for semi- or non-volatile analytes. In 2020, the organic solvent (CCl_4) as the adsorbent coating was used for the TFME method, increasing the efficiency of the analyte preconcentration [27]. The IMS responses of the extracted target analyte before and after coating were improved about 12 times. Evaporation of the thin film coating during the extraction was also remained as the principal problem of the method.

The aim of this method was hyphenating the DLLME method with cooling-assisted organic solvent-coated TFME to improve the extraction efficiency and enrichment factor of chlorpyrifos (as a model compound). The nickel foam was applied as the thin film and the corona discharge ionization source-ion mobility spectrometry (CD-IMS) apparatus was also utilized to determine the analyte compound. The commercial nickel foam as a substrate for holding the organic solvent has a high thermal conductivity (1.1315 $W\ m^{-1}\ k^{-1}$) and a high porosity (97 %, 110 pores per inch). In addition, the high mechanical stability of the nickel foam can increase the number of times that it may be used, without any damage. The thickness and contact area of the film were increased by organic solvent coated on the thin film, resulting in a significant improvement in the extraction efficiency compared to TFME or SDME alone. In this configuration, a uniform cooled temperature is only applied to the thin film, which leads to no condensation of analyte on other regions in the extraction chamber and protection of organic solvent, increasing the analyte extraction on the thin film. Using these two steps of analyte extraction improves the cleaning-up and sample preconcentration compared to headspace TFME and DLLME alone and reduces the interference of the sample matrix. Moreover, using the organic solution obtained by the DLLME method instead of the aqueous sample containing analyte helps to increase the total vaporization of the sample. Finally, some effective variables were optimized to improve the extraction efficiency, and different real samples were analyzed to show the method capability.

2. Experimental

2.1. Reagents and standards

Chlorpyrifos pesticide (98 % purity) was purchased from Kavosh Kimia Kerman Co. (Kerman, Iran). Methanol, ethanol, and acetonitrile (all HPLC grade) were provided from Sigma-Aldrich Co. (St. Louis, USA). Dichloromethane (CH_2Cl_2), toluene, and tetrachloromethane (CCl_4) were prepared from Merck Co. (Darmstadt, Germany). Trichloromethane ($CHCl_3$) was purchased from Riedel-de Haen Co. (Germany). N-hexane was prepared from Dr. Mojallali Industrial Chemical Complex Co. (Tehran, Iran). Cyclohexane was purchased from Honeywell Co. (Mexico City, Mexico). To prepare the Britton–Robinson buffer, boric acid (H_3BO_3, 99.8 % purity), acetic acid (CH_3COOH, glacial), phosphoric acid (H_3PO_4, 85 % purity), and Na_2SO_4 salt were prepared from Merck Co. (Darmstadt,

Germany). Nickel foam was purchased from Xiamen Tob New Energy Technology Co. (Xiamen, China).

2.2. Instrumentation

The used CD-IMS instrument was manufactured by Teif Azmon Espadana Co. (Isfahan, Iran). A thermal desorption unit was applied to evaporate and transfer the analyte vapor to the CD-IMS apparatus, and it was manufactured at Isfahan University of Technology (Isfahan, Iran) [28]. The applied parameters of CD-IMS are depicted in Table 1. All solid materials were weighted by a Sartorius scale (0.1 mg precision, TE 124S, Germany). The centrifuge device was prepared from Daytajhiz-ap Co. (model RST 16, Iran). A pH meter (Denver instrument, model UB-10, USA) was also applied to adjust the pH of the different samples.

2.3. Design of the extraction device

To combine the DLLME with the organic solvent coated TFME method, a new configuration was introduced. The collected phase obtained by the DLLME technique was reserved in a volumetric flask (25 mL). The volumetric flask was sealed and located in a stainless-steel chamber and the temperature was enhanced homogenously by a rod element with a length and diameter of 50.0 mm and 8.0 mm, respectively. The cooling system based on the condenser device was then designed to protect the volatile solvent coated on the film. The condenser placed on the top of the volumetric flask was made of a glass tube with a length of 70.0 mm and the inner and outer diameters of 7.0 mm and 15.0 mm, respectively. To prevent the analyte vapor leakage, the interface between the condenser and the volumetric flask was sealed by sandpaper glass with a length of 15.0 mm and a silicon binder layer. The interface temperature was kept the same as that of the volumetric flask to prevent the condensing of the analyte in the interface wall. The nickel foam film with the dimensions of 5.0 mm $\times$ 5.0 mm was selected to extract the analyte by using the total vaporization procedure.

2.4. Preparation of real sample

For analyzing the analyte compound in real samples, different samples such as agricultural wastewater, well water, and potato were selected. The agricultural wastewater and well water were collected from Dowlat Abad (Isfahan, Iran) and Kharman Kooh (Fasa, Iran), respectively. The potato sample was purchased from a local supermarket. Before extracting the analyte, the pH of the potato and water samples were both adjusted to 2.0. The potato sample was chunked by a mixer and the homogenized sample (about 1 g) was mixed with 4.0 mL of the Britton–Robinson buffer (pH = 2.0). Then, the sample was spiked with the analyte at different concentrations levels. To overcome the matrix effect on the analysis of analyte, the samples were placed at the temperature of 45 °C for 20.0 min; afterward, they were centrifuged at a g-force of 1010 g for 10.0 min. Eventually, the clear upper solution was completely separated and mixed with buffer solution (pH = 2.0) by the ratio of 1:2, prior to the extraction process [19].

2.5. Extraction procedure

The schematic drawing of the proposed approach is shown in Fig. 1. To extract the analyte from a standard solution, 5.0 mL of the aqueous sample (analyte concentration; 0.5 μg L^{-1}, pH = 2.0) was prepared in a glass vial for the DLLME operation. Afterward, 100.0 μL of trichloromethane and 1.0 mL of methanol as the extraction and disperser solvents were mixed and injected into the aqueous solutions quickly, to form the cloudy solution. To separate the organic phase, centrifuging the cloudy solution was accomplished at 1010 g for 3.0 min. All the collected phase volume was delivered into a 25-mL volumetric flask at the temperature of 120 °C, equipped with the condenser cooling system. The nickel foam film (5.0 mm $\times$ 5.0 mm) was chosen and immersed into the cyclohexane solvent to fill the thin film porosity. Then, the sorbent supported by cyclohexane was transferred into the condenser and the total vaporization procedure was accomplished for 20.0 min. For analyzing the target compound, the thin film was transferred quickly into the introduction system of the CD-IMS apparatus.

Table 1
Applied parameters of the CD-IMS.

Parameter	Setting
IMS Mode	Positive
Needle voltage	4.0 kV
Target electrode voltage	7.5 kV
Drift electric field	420 V cm^{-1}
Drift gas flow (N_2, 99.999 %)	1000 mL min^{-1}
Carrier gas flow (N_2, 99.999 %)	800 mL min^{-1}
Temperature of IMS cell	160 °C
Temperature of TDU	220 °C
Drift tube length	11 cm
Shutter grid pulse	300 μs
Shutter grid voltage	170 V
Shutter grid frequency	25 Hz
Number of IMS averages	25
Number of points per ion mobility spectrum	500

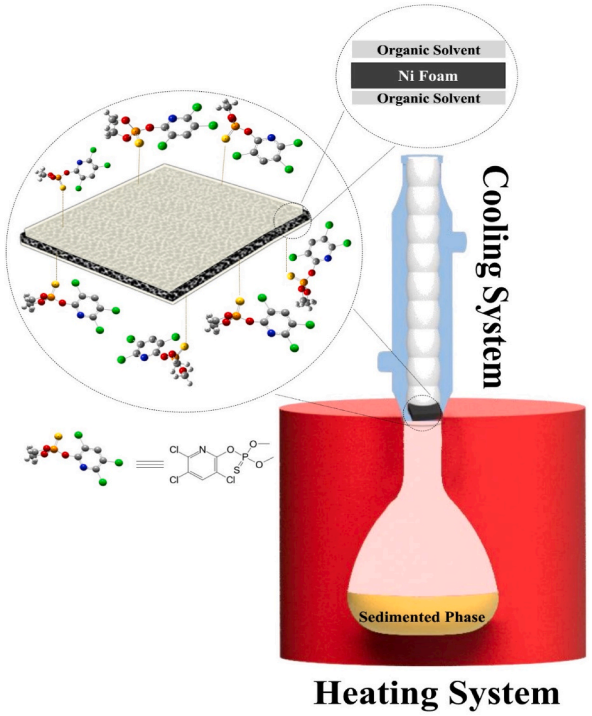

Fig. 1. Schematic diagram of the DLLME-cooling assisted organic solvent-coated TFME method.

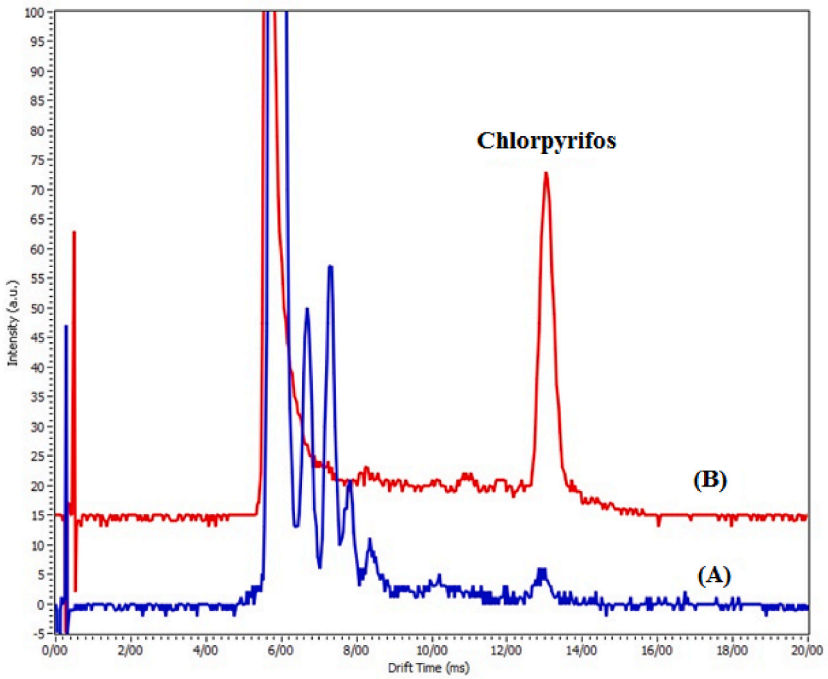

Fig. 2. The ion mobility spectra of the analyte extracted (analyte concentration, 20.0 μg L^{-1}) by A) DLLME and B) DLLME-cooling assisted organic solvent-coated TFME methods.

3. Results and discussion

3.1. Performance of the extraction method

To establish the effectiveness of the proposed approach as a novel pretreatment method, two experiments were carried out, separately. Firstly, 5.0 mL of the aqueous solution (analyte concentration; 20.0 μg L^{-1}, pH = 7.0) was prepared. Then, 1.0 mL of methanol and 100.0 μL of tetrachloromethane were mixed and injected into the aqueous solution for the DLLME operation. After centrifugation, the sedimented phase was injected into the CD-IMS apparatus. In another experiment, the sedimented phase obtained by the DLLME method was separated and transferred into the 25-mL volumetric flask at the temperature of 100 °C. The nickel foam with the dimensions of 5.0 mm × 5.0 mm was chosen as a porous thin film and immerged into the tetrachloromethane solvent to be saturated the thin film. The thin film supported by organic solvent was transferred into the cooling system for the TFME operation at headspace (for 20.0 min). The thin film was finally injected into the thermal desorption system of the CD-IMS apparatus for analyzing the target compound. It should be mentioned that all applied conditions for the DLLME method were similar to those of the first experiment. The extracted analyte signals in IMS (concentration; 20.0 μg L^{-1}) were shown in Fig. 2-A) DLLME and Fig. 2-B) DLLME-cooling assisted organic solvent-coated TFME methods. As can be observed, the signal was improved considerably (~28 times), when the cooling assisted organic solvent coated TFME was used after the DLLME method. In the DLLME-CD-IMS (method A), a low volume of the sedimented phase could be injected into the apparatus, limiting the IMS signal of the analyte. In fact, it is problematic to inject the total volume of the sedimented phase into the CD-IMS due to the competitive effect between analyte and solvent molecules in the ionization source. While in the proposed approach (method B), the sedimented phase was completely employed to extract the analyte, improving the CD-IMS sensitivity. The thickness and contact area of the thin film were increased by using the solvent placed on the film surface relative to TFME or SDME alone; therefore, the analyte molecules were extracted more effectively into the thin film. The condenser, as a cooling system for the thin film, was applied to prevent the organic solvent evaporation and condense of the analyte molecules on the film surface, increasing the distribution coefficient of the analyte.

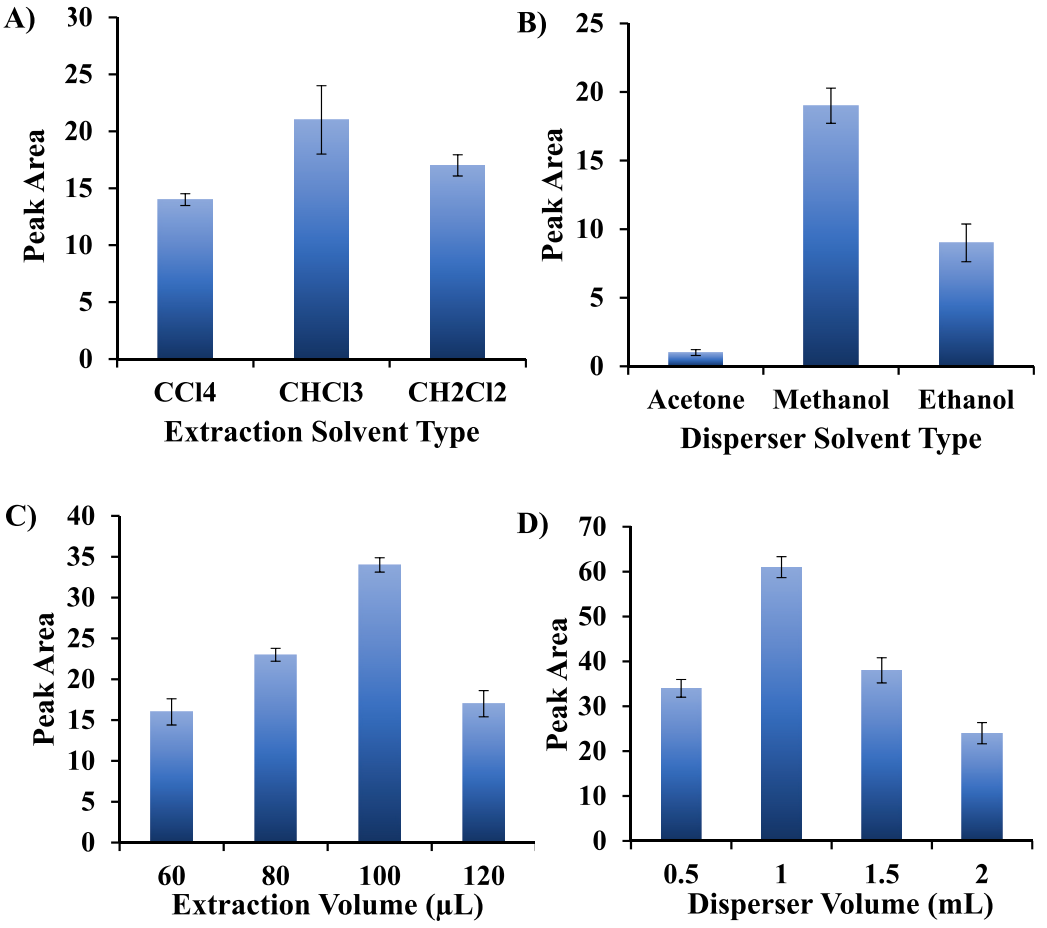

Fig. 3. The effect of A) extraction solvent type, B) disperser solvent type, C) extraction volume, and D) disperser volume on the extraction efficiency (sample volume; 5.0 mL, concentration of analyte; 10.0 μg L^{-1}).

3.2. Optimization of the extraction parameters

To obtain a high extraction efficiency by the proposed method, some effective parameters, including extraction and disperser solvent types and their volumes, sample pH, organic solvent type, ionic strength, extraction temperature, centrifugation time, and extraction time were studied and optimized.

3.2.1. Extraction solvent type

The extraction solvent type is an effective variable for the extraction of analyte by the proposed method. In this regard, some organic solvents with different solubilities in water such as CH_2Cl_2, $CHCl_3$, and CCl_4 were selected. After extracting by the DLLME method, the sedimented phase was totally used to carry out the TFME method. Fig. 3-A demonstrates the influence of the extraction solvent type on the analyte extraction. According to this figure, the highest extraction efficiency was obtained for $CHCl_3$. This might be due to the solubility of chlorpyrifos in CH_2Cl_2, $CHCl_3$, and CCl_4 solvents (400, 630, and 310 g per 100 g solvent, respectively). Therefore, analyte has the highest solubility in $CHCl_3$, resulting in more efficiency of the extraction.

3.2.2. Disperser solvent type

The disperser solvent was selected based on the miscibility in the organic and aqueous solutions. The creation of small droplets of the extraction solvent for increasing the contact area with the analyte is another property of the disperser solvent that must be considered. In this regard, three disperser solvents, including methanol, ethanol, and acetone were selected. Based on the obtained results shown in Fig. 3-B, the best extraction efficiency was obtained when methanol was applied as a disperser solvent. In fact, the proton affinity values of methanol, ethanol, and acetone are reported 754.3, 779.4, and 812.0 kJ mol^{-1}, respectively. When the methanol with the lowest proton affinity is injected into the CD-IMS, the proton transfer is easier done to ionize the analyte, improving the IMS signal. On the other hand, in the presence of methanol, $CHCl_3$ is dispersed well to form the cloudy solution, increasing the contact area between analyte and extraction solvent molecules.

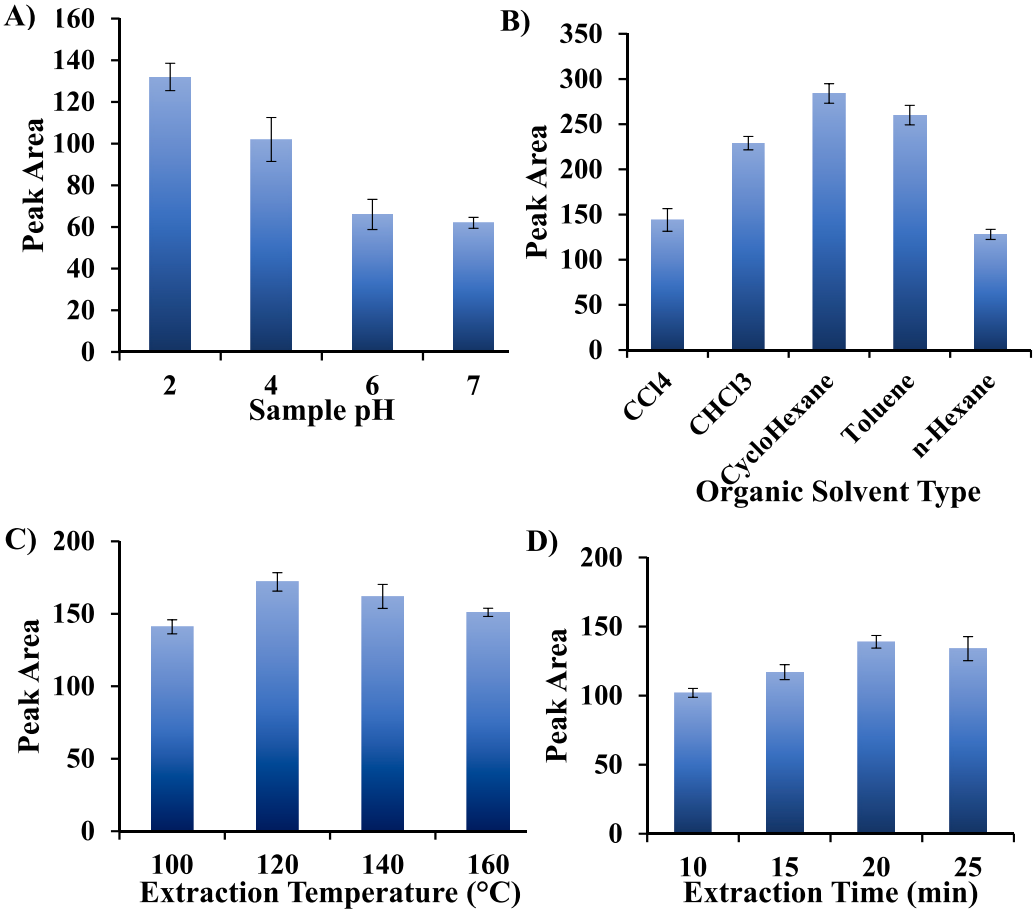

Fig. 4. The effect of A) sample pH, B) organic solvent type, C) extraction temperature, and D) extraction time on the extraction efficiency by the proposed method (sample volume; 5.0 mL, concentration of analyte; 10.0 μg L^{-1}).

3.2.3. Extraction volume

Another important variable in the extraction of analyte is the extraction solvent volume. Different volumes of $CHCl_3$, 60.0, 80.0, 100.0, and 120.0 μL, were mixed with 0.5 mL methanol. The mixture solvent was injected into the aqueous solution (5.0 mL) to perform the DLLME procedure before the TFME method. According to Fig. 3-C, the extraction efficiency was improved by increasing the $CHCl_3$ volume up to 100.0 μL; afterward, it was diminished. In fact, the distribution coefficient of the analyte was increased at the lower volumes of the extraction solvent (lower than 100.0 μL), due to a lower amount of the extraction solvent droplets in the solution. On the other hand, the IMS signal of the analyte was decreased at higher than 100.0 μL of extraction solvent due to the dilution effect.

3.2.4. Disperser volume

To find out the impact of the disperser volume on the extraction of the chlorpyrifos molecules, different volumes of methanol, 0.5, 1.0, 1.5, and 2.0 mL, were studied. According to Fig. 3-D, the highest efficiency of the extraction was found when 1.0 mL methanol was used as a disperser volume. It is notable that the cloudy solution could not be created at the lower disperser volumes (<1.0 mL). In addition, the solubility of $CHCl_3$ in the water sample was enhanced at higher disperser volumes, so the extraction of the analyte was decreased with more than 1.0 mL of disperser solvent.

3.2.5. Sample pH

Another crucial variable that affected the analyte extraction is sample pH. Different solutions with pH values of 2.0, 4.0, 6.0, and 7.0 were prepared by Britton–Robinson buffer. Fig. 4-A shows the effect of the sample solution pH on the extraction yield, indicating the highest extraction of chlorpyrifos molecules was picked up at pH = 2.0. Generally, the optimized pH of the analyte solution was related to the p*K*a of the analyte. The p*K*a of chlorpyrifos is 5.1 [29]; so, the neutral form of this compound is produced in a highly acidic solution, increasing the extraction efficiency. More ionized form of analyte is obtained at the sample pH higher than 5.1, reducing the extraction of the analyte to the organic phase.

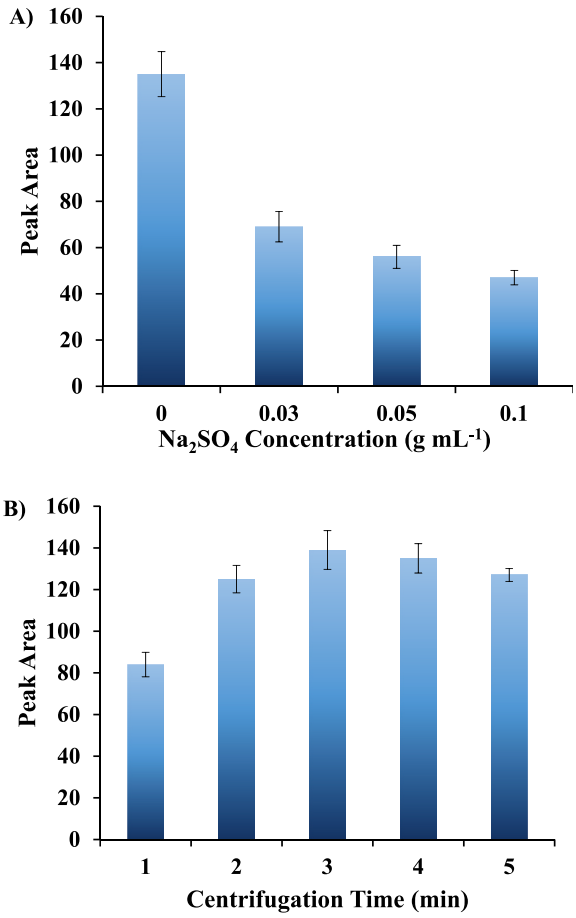

Fig. 5. The effect of A) ionic strength and B) centrifugation time on the extraction efficiency by the proposed method (sample volume; 5.0 mL, concentration of analyte; 10.0 μg L^{-1}).

3.2.6. Type of the organic solvent coated thin film

The type of organic solvent not only affects the extraction yield, but also disturbs the ionization of the analyte in the positive mode of CD-IMS apparatus due to the competitive nature of the proton transferring of the ion-molecules gas-phase reactions in the ionization source. This could impact the sensitivity of the CD-IMS system. Therefore, an appropriate organic solvent with minimum interferences should be chosen for coating the thin films. To that end, five different solvents, including CH_2Cl_2, $CHCl_3$, CCl_4, n-Hexane, and cyclohexane, were studied as the support of the thin film. Fig. 4-B depicts the IMS signal against the extracted analyte for each organic solvent. Considering these results, the best extraction efficiency was achieved when the thin films were coated with cyclohexane.

3.2.7. Extraction temperature

In the headspace TFME method, the temperature is an important variable for controlling the analyte extraction. In this work, the extraction temperature was selected as adequate to achieve the total vaporization of the sample solution. To that end, different temperatures of 100, 120, 140, and 160 °C were investigated. Based on the results, a maximum response of IMS was obtained at the temperature of 120 °C (as seen in Fig. 4-C). It was expected that the IMS signal was almost constant at the higher temperature of 120 °C due to the equilibrium state between the thin film and the vapor phase. However, the organic solvent coated on a thin film might be evaporated at higher temperatures (>120 °C), reducing the extraction efficiency.

3.2.8. Extraction time

In the headspace TFME method, the highest extraction of the analyte could be achieved in the equilibrium time, as clarified by Nernst's partition law [30]. In this regard, different extraction times of 10.0, 15.0, 20.0, and 25.0 min were selected and evaluated to reach the equilibrium time. Fig. 4-D indicates the effect of the extraction time on its efficiency for the analyte molecules. Based on these results, the highest response of IMS was observed for 20.0 min.

3.2.9. Ionic strength

To achieve the optimum ionic strength, the effect of different concentrations of Na_2SO_4 (0, 3, 5, and 10 (w/v%)) on the analyte extraction was investigated. The obtained results presented in Fig. 5-A indicate that the extraction efficiency of the analyte was reduced when Na_2SO_4 salt was added to the aqueous sample. This might be due to increasing the solution viscosity and electrostatic effect in the presence of the salt.

3.2.10. Centrifugation time

The centrifugation time depends on the equilibrium time between aqueous and organic phases. In this regard, different times of the centrifuge (1.0, 2.0, 3.0, 4.0, and 5.0 min) were studied, and the effect of the centrifugation time on the extraction yield is shown in Fig. 5-B. Based on this figure, when the centrifugation time was raised, the extraction of analyte was increased until the equilibrium state was achieved. Therefore, the highest extraction efficiency was achieved at 3.0 min.

3.3. Thin film durability

To investigate the stability and lifetime of the nickel foam, a commercial nickel foam with high mechanical stability was selected and utilized as a thin film more than 140 times. On the other hand, this sorbent was also used as an organic solvent holder without any considerable reduction in the extraction efficiency. Under the same conditions, the nickel foam stability was examined by the comparison between the responses obtained by a new film for the extracted analyte in distilled water and that obtained after 140 times extraction by a thin film. Based on the statistical results, the experimental and critical t values (at CL = 95 %, df = 4) were calculated 1.04 and 2.77, respectively, indicating no significant difference between the extraction results of two nickel foams.

3.4. Analytical variables

To obtain the highest efficiency of extraction, the optimized conditions ($CHCl_3$ as the extraction solvent, methanol as the disperser solvent, extraction volume; 100.0 μL, disperser volume; 1.0 mL, sample pH; 2.0, centrifugation time; 3.0 min, cyclohexane as the organic solvent coating on the thin film, extraction temperature; 120 °C, extraction time; 20.0 min, and without salt addition) were applied for the extraction of analyte molecules. At the mentioned conditions, the capability of the proposed method was evaluated for analyzing the analyte and different analytical variables such as limit of quantification (LOQ), linear dynamic range (LDR), repeatability index, coefficient of determination (R^2), and limit of detection (LOD) were obtained in the pure water spiked with the different analyte concentrations (0.1–10.0 μg L^{-1}). At the same conditions, the least square method was applied to plot the calibration curve, resulting a LDR between 0.1 and 7.0 μg L^{-1} with the determination coefficient of 0.9997. The calculated LOD (S/N = 3) and LOQ (S/N = 10) were 0.03 and 0.1 μg L^{-1}, respectively. At the analyte concentrations of 0.1, 3.0, and 7.0 μg L^{-1}, the relative standard deviations (RSDs), as a repeatability index, were determined 6 %, 5 %, and 4 % for intra-day and 9 %, 6 %, and 5 % for inter-day, respectively. The enrichment factor (EF) was computed to be 3630 (chlorpyrifos concentration; 1.0 μg L^{-1}). Based on Eq. (1), the EF was calculated by dividing the analyte concentration after extracting by the proposed method (C_{sed}) to its initial concentration (C_0).

$$EF = \frac{C_{sed}}{C_0} \tag{1}$$

3.5. Real samples analysis

To study the capability of the DLLME-cooling assisted organic solvent coated TFME method to extract of analyte in the complex matrix, well water, agricultural wastewater, and potato samples were selected and analyzed as the real samples. To reduce the matrix effect and quantify chlorpyrifos as the target analyte, a multiple standard addition method was applied. In the mentioned method, different volumes of a known analyte concentration (C_s) were prepared and injected into the multiple portions of sample solution with the same volume (V_x). After extraction process, the analyte responses of the mentioned solutions were plotted versus the different volumes of a known standard concentration. Then, the obtained line was extrapolated to a zero signal and the analyte volume in the unknown sample (V_{xs}) was calculated. Based on the Eq. No. 2, the initial analyte concentration in the unknown sample solution was obtained.

$$C_x = \frac{C_s V_{x_s}}{V_x} \tag{2}$$

According to the obtained results tabulated in Table 2, the analyte concentrations in the agricultural wastewater and well water samples were 2.04 and 3.25 μg L^{-1}, respectively. However, for the potato sample, the analyte concentration was less than the LOD of the proposed approach. To study the accuracy of the described method, the relative recovery (RR%) values were also calculated at the analyte concentration levels of 3.0 μg L^{-1}, 1.5 μg L^{-1}, and 25.0 μg kg^{-1} for agricultural wastewater, well water, and potato samples, respectively. The RR% values were obtained based on Eq. (3).

$$RR\% = \frac{C_{Found} - C_{Real}}{C_{Added}} \times 100 \tag{3}$$

Where C_{Real} and C_{Found} are the analyte concentrations before and after adding the standard analyte solution to the real samples, respectively and C_{Added} is the analyte concentration spiked to the real samples. Accordingly, the RR% values were calculated between 92 % and 99 %. The extracted analyte responses in IMS were shown in Fig. 6-A) agricultural wastewater and Fig. 6-B) well water before and after spiking analyte with the concentration of 3.0 μg L^{-1}. Therefore, the DLLME coupled with cooling assisted organic solvent coated TFME method could be introduced as an appropriate methodology to analyze the analyte in environmental and foodstuff samples. The evaluation of the method accuracy was carried out by the analyte determination in the well water using European Standards EN 12393 method. The residue of the analyte in the real sample was extracted and measured by gas chromatography (GC). The analyte found for the spiked real sample (20 μg L^{-1}) using standard GC and the proposed methods are 17 ± 2 and 19 ± 2 μg L^{-1}, respectively. Based on the statistical results, the experimental and critical t values (at CL = 95 %, df = 4) were obtained 1.22 and 2.77, respectively, indicating no significant difference between the results of two methods.

3.6. Evaluation of matrix effect

Based on Eq. (4), the matrix effect (ME%) was calculated.

$$ME\% = \left(\frac{S_M}{S_s} - 1\right) \times 100 \tag{4}$$

Where S_M and S_S are the signals of the target analyte after extracting in the matrix sample and solvent, respectively. The obtained matrix effect values are shown in Table 2. A positive and negative amount of matrix effect indicates a higher and a lower analyte response in the matrix samples than in the solvent, respectively [31,32].

3.7. Comparison of the proposed method with other methods

Some figures of merit, such as LOD, LDR, EF, RSD, and RR% values of the proposed method were compared with those reported in other studies focusing on the extraction and determination of chlorpyrifos, as shown in Table 3. As be observed, some variables of the developed method are better or comparable relative to those reported by other methods. According to this Table, the LOD, EF, and RR

Table 2
Analysis of chlorpyrifos compound in real samples using proposed method.

Sample	Added[a]	Found[a]	Relative recovery (%)	Matrix effect (%)
Agricultural wastewater	–	2.04	–	−20
	3.0	4.92 (2)[c]	96 (4)[c]	−26
Well water	–	3.25	–	−11
	1.5	4.63 (3)	92 (9)	−17
Potato	–	ND[b]	–	–
	25.0	24.82 (6)	99 (6)	−23

[a] The analyte concentration (μg L^{-1} for water samples and μg kg^{-1} for potato sample).
[b] Not detected.
[C] Relative standard deviation (%).

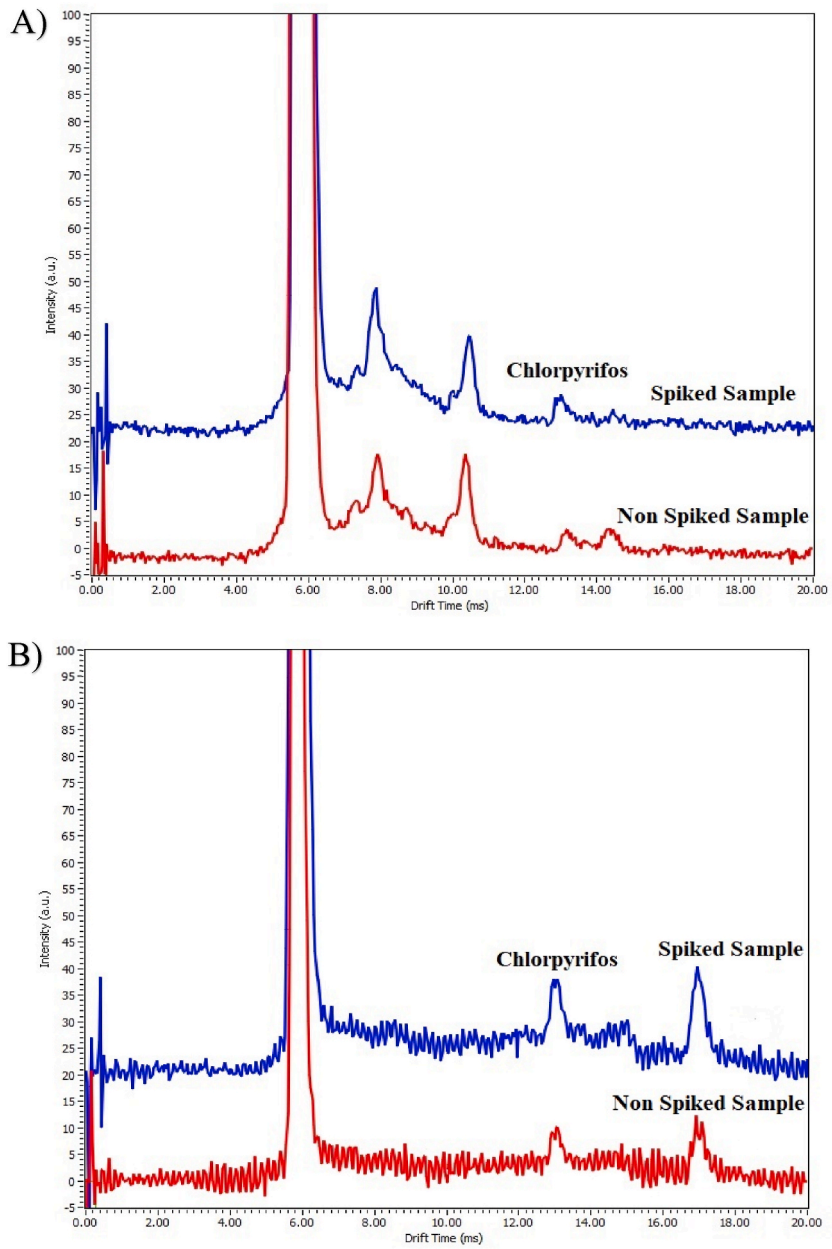

Figure 6

Fig. 6. The ion mobility spectra of the extracted chlorpyrifos from A) agricultural wastewater and B) well samples (The analyte concentration spiked to water samples is 3.0 μg L^{-1}).

% values of this method were superior at comparing with MISPE-GC-MS, SPME-CD-IMS, DSPE-DLLME-HPLC, MA–HS–SPME-GC-ECD, DLLME-GC-FPD, and TFME-CD-IMS methods [33–38]. Despite a lower LDR in this method relative to SPE-LC-MS/MS, MNPs-HPLC-UV, HS-SPME-GC-NPD, and MA–HS–SPME-GC-ECD methods [35,39–41], the proposed method is cheap, simple, and rapid with low maintenance and no need for the vacuum. In many laboratories, chromatographic-based methods including GC and HPLC have been developed spatially for the analysis of multi-analyte samples. However, these techniques have serious drawbacks such as long response time, derivatization for some compounds, water interferences in the GC method, and using the large volume of expensive and environmentally harmful solvents. Consequently, the obtained results indicate that the proposed method could be used successfully as an alternative technique for the extraction and quantification of analyte.

Table 3
Comparison of DLLME-cooling assisted organic solvent coated TFME-CD-IMS method with other methods.

Method	Sample type	LDR[a] (μg L^{-1})	LOD[b] (μg L^{-1})	EF[c]	RSD[d] (%)	Relative recovery (%)	Reference
TFME-CD-IMS	River water, agricultural wastewater	2–200	0.6	–	4–7	96–109	[33]
DLLME-GC-FPD[e]	Tap water, lake water, river water, farm water and well water	2.00–160	0.57	795	8.5	83.9–92.0	[34]
MA–HS–SPME[f]-GC-ECD	Urine	0.1–500	0.0832	–	0.7–8.4	99–104	[35]
DSPE[g]-DLLME-HPLC	Urine	5–400	1.2	235	1.9–3.7	95–101	[36]
SPME-CD-IMS	River and well water, Agricultural wastewater, grape, tangerine	0.1–10	0.05	–	2.7–3.9	86–117	[37]
MISPE-GC-MS	River water	0.1–7.5	0.05	–	<10	88–93	[38]
SPE-LC-MS/MS	Urban wastewater	0.0011–1.6	1.44 (ng L^{-1})	–	6.6	115	[39]
HS-SPME-GC-NPD	Water and soil	0.025–50	0.008	–	5.9–10.1	88–108	[40]
MNPs[h]-HPLC-UV	River water	100-15000 (ng L^{-1})	28.6 (ng L^{-1})	1000	2.4–8.7	88.5–96.7	[41]
DLLME-TFE[i]-CD-IMS	Well water, agricultural wastewater Apple, tomato	0.1–3.0 1.5–15 (μg kg^{-1})	0.04 0.562 (μg kg^{-1})	5395	3–7	99–103 107–111	[17]
Spectrofluorimetric	Pollen	1.43×10^{-9}- 7.13×10^{-9} (mol L^{-1})	4.40×10^{-10} (mol L^{-1})	–	–	102.6–104.2	[42]
Smart SPME-GC-FID	Wheat	200–4000 (μg kg^{-1})	20 (μg kg^{-1})	–	5.6–15	–	[43]
PEC[j]-Sensor	wastewater samples	0.05–500	0.017	–	4.3–5.9	93–106	[44]
CFI-MS[k]	tomato	–	83.3 nM	–	1.67–5.38	–	[45]
DLLME-Cooling Assisted Organic Solvent Coated TFME-CD-IMS	Agricultural wastewater, well water potato	0.1–7.0 5.0–50.0 (μg kg^{-1})	0.03 1.5	3630	5–9	92–96 99	This work

[a] Linear dynamic range.
[b] Limit of detection.
[c] Enrichment factor.
[d] Relative standard deviation.
[e] Flame photometric detector.
[f] Head space-solid phase microextraction.
[g] Dispersive solid-phase extraction.
[h] Magnetic nanoparticles.
[i] Thin film evaporation.
[j] Photoelectrochemical.
[k] Carbon fiber ionization-mass spectrometry.

4. Conclusions

The DLLME-cooling assisted organic solvent-coated TFME method was introduced as a novel sample preparation method for the extraction of chlorpyrifos compound before determining by CD-IMS apparatus. The headspace TFME may be applied for more volatile compounds and considerably enhances the number of times of film usage. The cyclohexane-coated thin film could show a high contact area with the vapor phase, increasing the extraction efficiency. In addition, the cooling device was applied to protect the organic solvent and condense of analyte on the thin film surface. In this regard, the distribution coefficient of the analyte between the thin film and the vapor phase was enhanced. Owing to the uniform cooled temperature of the thin film, the analyte was not condensed on the other regions in the extraction setup and concentrated only on the thin film. The proposed method showed a better preconcentration factor and cleaning-up due to using of two steps of analyte extraction, reducing the matrix interferences. The proposed method was introduced as an accurate, sensitive, and reliable method with a high enrichment factor for determining different chemical compounds in different matrices. Although the proposed extraction method is not selective for analyzing other pesticides or any other pollutants, the values of drift time may be considered as a separation parameter in the detection system of IMS. No solvent interference and high extraction efficiency are the significant advantages of the studied method; but, the method is limited to analyze volatile chemical compounds.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Mohammad R. Rezayat: Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Mohammad T. Jafari:** Writing – review & editing, Project administration, Conceptualization. **Leila Mohammadipour:** Writing – original draft, Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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