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Design of an ultrasonic piezoelectric injection port for analysis of thermally unstable compounds using corona discharge ion mobility spectrometry

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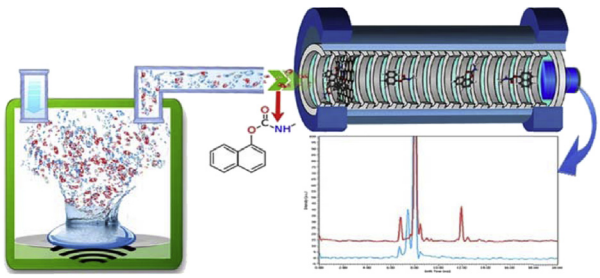
HIGHLIGHTS

- A novel injection port based on the ultrasonic nebulization was designed and constructed for CD-IMS.
- This system expanded the instrument application toward the analysis of thermally unstable compounds.
- The extracted carbaryl could be analyzed, directly, without any tedious derivatization.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports on a novel ultrasonic injection port designed and constructed to analyze thermally unstable chemical compounds using corona discharge ion mobility spectrometry (CD-IMS). In order to achieve the highest possible efficiency with the device, some parameters such as the solvent type, carrier gas flow rate and sample volume were exhaustively investigated. Through a comparative study conducted, it was revealed that unlike the thermal desorption system, the proposed ultrasonic injection port could easily be used for the analysis of some thermally unstable compounds such as carbaryl, propoxur and vitamin B_1, by means of CD-IMS. To evaluate the potential of the device, carbaryl, extracted from different samples by dispersive liquid-liquid microextraction technique, was quantitatively analyzed. The CD-IMS-based results brought forth the detection limit of 0.03 mg L^{-1}, and dynamic range of 0.1 −10.0 mg L^{-1} with the determination coefficient of 0.9981. The relative standard deviations for one day and three consecutive days were 4 and 6%, respectively. Further, the spiked samples of agricultural wastewater, underground water, and tomato analyzed culminated in the recovery values of 83%, 98% and 82%, respectively. The satisfactory results proved an acceptable capability of the sample introduction system, to be conveniently used for routine analysis of thermally unstable compound, without any tedious derivatization.

1. Introduction

The technique of ion mobility spectrometry (IMS) was introduced with the name of “plasma chromatography” in 1970, by Cohen and Karasek [1]. In IMS, the sample is first converted into the

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ionic species *via* an ionization source and then the ions are separated based on their different mobility values in an electric field [2]. The mobility of the ions is dependent on their mass, charge, and shape. So, one of the advantages of IMS related to mass spectrometry is its capability in the analysis of isomeric species which is very helpful in the proteomics researches. This method has other advantages such as high sensitivity, portability, ease of maintenance, high speed of analysis, and low cost. That is why IMS has been utilized as an analytical instrument for analysis of various chemical compounds including explosives, narcotics, pesticides, and drugs [3–6].

Several ionization sources such as radioactive materials [7], corona discharge [8], electrospray [9], low temperature plasma [10], laser ablation [11], and surface ionization [12] have been used in IMS. Among these ionization methods, electrospray is considered as the soft ionization technique for direct analysis of thermally unstable chemical compounds (e.g. biomolecules), in liquid samples [13]. However, this ionization source suffers from several drawbacks such as reliance on special pumps and solvents. In addition, perturbation of the electrospray process and needle clogging could not be avoided if the method of sample preparation is inefficient [10]. So, electrospray could not be considered as a suitable candidate for routine field analysis of unstable compounds by IMS. On the other hand, ^{63}Ni and corona discharge, as the most popular ionization sources, have been widely used for the analysis of chemical compounds in gaseous phase [2,14]. Using these ionization sources, samples must be vaporized, prior to entering the ionization source. One of the best methods for evaporation of samples is thermal desorption technique. To date, several injection ports, based on the thermal desorption method, have been designed for IMS [15–17]. Considering these works, it can be concluded that the method of thermal evaporation is very simple and easy to use for the analysis of liquid and solid samples by IMS. However, as far as we know, some chemical compounds are thermally unstable, and so, degradation of these molecules could occur during the thermal evaporation process. Consequently, it is necessary to develop an alternative method for evaporation of thermally unstable analytes, before analyzing them by IMS with ^{63}Ni or corona discharge ionization source.

The ultrasonic nebulizer, based on piezoelectric effect, has been introduced several decades ago, as a portable nebulizer. The operation principle of an ultrasonic nebulizer is very simple. In this device, sample solution is placed onto the surface of piezoelectric transducer, coupled to an oscillator with RF frequency. This high frequency ultrasonic wave produces the vibration of a piezoelectric element which is in contact with liquid sample. The energy of this vibration is sufficient to very efficiently break up the liquid stream into very fine droplets (~10 μm diameter) [18,19]. So far, the piezoelectric nebulizers have been used as sample introduction before analyzing by different analytical instrument such as mass spectrometry [20], Raman spectroscopy [21], and inductively coupled plasma [22]. In 2011, Hugo et. Al [23] used an injector device based on piezoelectric actuation for calibration and control of dopant levels in IMS. However, to our knowledge, no paper has been published investigating the capability of piezoelectric nebulizer as the sample introduction system in IMS for quantitative analysis of compounds.

In this work, a novel sample introduction system based on ultrasonic piezoelectric nebulizer was designed, constructed, and used for corona discharge IMS. The device was successfully utilized to detect some thermally unstable chemical compounds, without any degradation. Different operation parameters affecting the efficiency of the introduction system were studied and optimized. Finally, the method was used for analyzing carbaryl (sevin) extracted from some matrices by dispersive liquid-liquid microextraction.

2. Experimental section

2.1. Chemicals and solvents

Methanol, acetone, acetonitrile, hexane, benzene, toluene, sodium chloride and hydrochloric acid were purchased from Merck (Darmstadt, Germany). All the solvents used for sample preparation and nebulization processes were HPLC grade. The standard materials of carbaryl (sevin) and propoxur insecticides were purchased from Accustandard, Inc. (U.S.A.). Thiamine (vitamine B1) with the purity of 98% was prepared from Kharazmi pharmaceutical Co., Karaj, Iran. The stock standard solutions of carbaryl were prepared in methanol and the standard working solutions were prepared on a daily basis by diluting the stock solution.

2.2. Ion mobility spectrometer

The corona discharge ion mobility spectrometer (CD-IMS) used in this study was designed and constructed at "Analytical Chemistry" laboratory, Isfahan University of Technology. The details of instrument have been reported in our previous paper [15]. Briefly, the IMS cell consists of three regions named ionization, reaction, and drift tube. In the ionization source, a corona discharge ionization source was used in the positive mode. In this region, a sharp needle was positioned 3 mm behind a counter electrode with a difference voltage of about 3.0 kV. Sample vapors were introduced into a tube of 30-mm length as the reaction region to react with reactant ions in the ionization source. This ionization region and drift tube region (110 mm length) were separated by means of a shutter grid (Bradbury-Nielsen type). After injection of the sample originated ions, they could be separated in the drift tube based on their mass, charge, and shape. In order to process the IMS date, special software was developed in the LabWiew. More detail about the software is presented in the Supporting Material. The thermal desorption sample introduction system used in the apparatus has also been described in detail, previously [15]. The mobility spectra were taken under the IMS operating conditions tabulated in Table 1.

2.3. Sample introduction system

In this research, the sample introduction system was designed based on the ultrasonic piezoelectric nebulization. Fig. 1 shows the schematic diagram of the constructed injection port and the way it is connected to the IMS cell. The main body of the injection port device was cylindrical and made of glass. The internal diameter and the height of this chamber were selected 30 and 20 mm, respectively. A circular piezoelectric element with 25 mm diameter and 2 mm thickness was fixed in a horizontal position at the bottom of chamber by means of a PTFE fixer. To close the chamber, a piece of

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

Operating parameters	Setting
Needle voltage	10.0 kV
Target electrode voltage	7.0 kV
Drift temperature	120 °C
Injection temperature	ambient
Drift field	400 V cm^{-1}
Drift gas flow (N_2)	1000 mL min^{-1}
Carrier gas flow (N_2)	80 mL min^{-1}
Drift tube length	11 cm
Shutter grid pulse	0.3 ms
Number of points per mobility spectrum	500

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