Journal of Chromatography A, 1343 (2014) 63–68

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Feasibility of corona discharge ion mobility spectrometry for direct analysis of samples extracted by dispersive liquid–liquid microextraction

Mohammad T. Jafari *, Farhad Riahi

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 4 March 2014
Accepted 27 March 2014
Available online 4 April 2014

Keywords:
Corona discharge ionization
Ion mobility spectrometry
Dispersive liquid–liquid microextraction
Malathion

ABSTRACT

The capability of corona discharge ionization ion mobility spectrometry (CD-IMS) for direct analysis of the samples extracted by dispersive liquid–liquid microextraction (DLLME) was investigated and evaluated, for the first time. To that end, an appropriate new injection port was designed and constructed, resulting in possibility of direct injection of the known sample volume, without tedious sample preparation steps (e.g. derivatization, solvent evaporation, and re-solving in another solvent. . .). Malathion as a test compound was extracted from different matrices by a rapid and convenient DLLME method. The positive ion mobility spectra of the extracted malathion were obtained after direct injection of carbon tetrachloride or methanol solutions. The analyte responses were compared and the statistical results revealed the feasibility of direct analysis of the extracted samples in carbon tetrachloride, resulting in a convenient methodology. The coupled method of DLLME-CD-IMS was exhaustively validated in terms of sensitivity, dynamic range, recovery, and enrichment factor. Finally, various real samples of apple, river and underground water were analyzed, all verifying the feasibility and success of the proposed method for the easy extraction of the analyte using DLLME separation before the direct analysis by CD-IMS.

1. Introduction

Preparation of samples can be considered as the most important steps in an analytical process and typically includes extraction, preconcentration, and cleanup of the sample. In fact, the sample preparation is generally required for the analysis of various chemical compounds in complex matrices [1]. So far, various sample preparation techniques including liquid–liquid extraction (LLE), solid-phase extraction (SPE), solid-phase microextraction (SPME), head space solid phase microextraction (HS-SPME), liquid-phase microextraction (LPME), and single-drop microextraction (SDME) have been used in the sample preparation of different chemical compounds. However, as most of these techniques are often complicated, expensive, and time consuming so the equilibrium could not be attained during a short time in most cases, thus limiting their applications for routine analysis. In addition, preparation of coating and short lifetime of the fibers, large sample volumes, high instrumentation cost, and low recovery are the main drawbacks of some of these methods. Nevertheless, all these sample preparation techniques have both advantages and disadvantages, having led to further developments in the sample preparation processes. In 1996, Assadi and co-workers developed an extraction technique named dispersive liquid–liquid microextraction (DLLME) [2]. The major advantages of the DLLME technique are simplicity of operation, rapidity, low cost, high recovery, and high enrichment factor (EF) [3]. These benefits are luring scientists to apply DLLME in the analysis of various compounds in different environmental and foodstuff samples [4–6]. Only in the last three years, several reviews have been published, demonstrating the significance of this sample preparation method [3–11]. Briefly speaking, in this sample preparation technique, a cloudy solution is formed by fast addition of the mixture of extracting and disperser solvent to an aqueous sample. The dispersion solvent must be soluble in both aqueous phase and extraction solvent. However, the extraction solvent which has a high potential for taking out the analyte must be soluble in the dispersion solvent while its solubility in water has to be very low. The cloudy state originates from the formation of fine droplets of the extraction solvent dispersed in the sample solution [10]. After centrifugation, the dispersion solvent is removed and the organic extraction solvent containing analyte can be accumulated in upper or lower layers based on its density, compared to the aqueous phase. Typically, the resultant sedimented phase or supernatant

* Corresponding author. Tel.: +98 311 391 2351; fax: +98 311 391 2350.
E-mail address: jafari@cc.iut.ac.ir (M.T. Jafari).

http://dx.doi.org/10.1016/j.chroma.2014.03.069
0021-9673/

can be analyzed by gas chromatoghraphy (GC) [12–15] or high performance liquid chromatography (HPLC) with various detectors [16–18]. However, these chromatographic methods require a long run time for separation in a column, reducing the detection speed in analysis progress. Of course, one needs to bear in mind that all the HPLC methods so far reviewed suffer from gradient elution using expensive solvents. On the other hand, the detection methods based on GC are limited to volatile compounds, unless a tedious and laborious derivatization procedure is followed before the analysis [19,20]. To overcome some possible problems in chromatographic methods, DLLME with other extraction methods such as SPE [21] and SBSE [22] has also been combined, however with complication in the analysis method.

Ion-mobility spectrometry (IMS) is an analytical technique used to separate and identify ionized molecules in the gas phase based on their mobility in a buffer gas. IMS is a significant analytical method for scientists because of its portability, speed, low cost, ease of maintenance, and low detection limits (~ppb). Compared with MS, the major benefit of IMS is that it can help users to distinguish between isomeric species due to its unique ability to separate ions on the basis of their shape [23]. Notwithstanding the significance of the method, the effects of other compounds in a sample on the IMS response to the target analyte complicate the interpretation of data. To elaborate, one of the immediate problems of the IMS instrument alone is matrix interference, especially in real sample analysis [24]. Consequently, an appropriate sample preparation step is necessary to extract trace levels of analytes, bring them to a suitable concentration levels, and remove the interferences in the matrix before the analysis. As mentioned above, DLLME has almost the same properties; nevertheless, it is necessary to be coupled to IMS so that its benefits of rapidity and convenience remain available as an added merit for DLLME-IMS method.

In this paper, the combination of DLLME and corona discharge ionization-ion mobility spectrometry (CD-IMS) was evaluated for the first time. In this regard, a new injection port was designed and constructed and was used for introduction of extracted sample into the CD-IMS cell. The test compound of malathion (as an organophosphoruse pesticide) was extracted by DLLME procedure and sedimented phase was directly injected into the injection port. Some parameters affecting the extraction efficiency such as the type and volume of extracting solvent, type and volume of disperser solvent, and salt addition were studied. The proposed method was applied to determine malathion pesticide residue in the apple and water samples.

2. Experimental

2.1. Standard solutions and reagents

Malathion (99% purity grade) was obtained from Accustandard Inc. (USA). All of the reagents used in this study such as dichloromethane, trichloromethane, carbon tetrachloride, methanol, acetonitryl, and aceton were analytical grade and purchased 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 standard stock solution using distilled water.

2.2. Injection port design

In this work, an appropriate new injection port was designed and constructed, helping us to have the possibility for direct injection of sample solutions into the ionization source of CD-IMS. Fig. 1 shows the schematic diagram of the injection port which was made

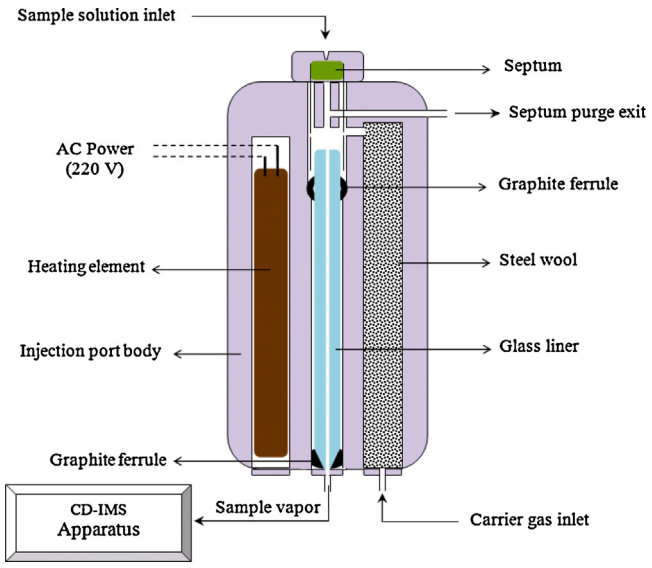

Fig. 1. Schematic diagram of the injection port designed for direct injection of liquid sample into the CD-IMS.

of stainless steel. In this design, heating element, hot line for warming up the carrier gas, and sample vapor generation region (glass liner) were embedded in an integrated device. A 200-W rod heating element was used to increase the temperature of the injection port device. The carrier gas passes through the hot line filled by steel wool for better heat transferring. The injection port was equipped with a digital temperature controller (Hanyoung, ED6, Korea). The sample solution can be transferred into the device using a microsyringe and through the septum implanted in the inlet port. The analyte is evaporated inside a glass liner (i.d. 1 mm) and its vapor can be transferred into the CD-IMS cell by preheated carrier gas.

2.3. Ion mobility spectrometry

The ion mobility spectrometer (IMS) used for this research was designed and constructed at Isfahan University of Technology as described previously [25]. In this work, however, the corona discharge ionization in the positive mode was applied as an ionization source. In brief, the main parts of the instrument include the following: the IMS cell, two high voltage power supplies, a pulse generator, an analog to digital converter and a computer. In this work, the IMS cell of the system was constructed from 16 aluminum rings 10 mm wide. These conducting rings were separated from each other by thin PTFE rings (1 mm in width). The aluminum rings were connected by a series of resistors to form the electric field gradient. The IMS cell length was divided into two regions, the ionization region including the corona discharge needle and the drift region (11 cm in length). The ionization and drift regions were separated from each other by means of a Bradbury-Nielsen grid. This shutter grid was made of two series of parallel wires biased to a potential, creating an orthogonal field relative to the drift field, to block ion passage to the drift tube. The grid potential was removed for a short period of time by the pulse generator to admit an ion pulse to the drift region. Generally, this period of time was selected 200 μs. Preheated nitrogen was employed as the drift and the carrier gases, with flow rates of 800 and 400 mL min^{-1}, respectively. The default Faraday plate detector configuration consisted of a 21 mm-diameter stainless steel plate positioned ~1.0 mm behind the aperture grid. A home-made preamplifier with the gain of 1×10^{10} V A^{-1} was used and then, the signal was further amplified up to 1000 times using a tunable-gain amplifier. Afterward, the signal was processed using a 12-bit analog to digital interface