



Cooling-assisted microextraction: Comparison of techniques and applications



Ali Reza Ghiasvand^{*}, Somayeh Hajipour, Nahid Heidari

Department of Chemistry, Lorestan University, Khoramabad, Iran

ARTICLE INFO

Keywords:

Cooling-assisted microextraction
Solid-phase microextraction
Liquid-phase microextraction
Thermoelectric cooler
Gas purge microsyringe extraction
Solid-phase dynamic extraction

ABSTRACT

Over the last decades, a special attention was given by the scientists to the cooling-assisted approach in many analytical methods, including solid-phase microextraction (SPME), liquid-phase microextraction (LPME), gas purge microsyringe extraction (GP-MSE), and solid-phase dynamic extraction (SPDE). Compared to conventional microextraction, the CA-ME strategy led to more effective methods, regarding extraction efficiency and their applicability to different sample matrices.

All CA-ME systems which have been reported to date were reviewed and their important aspects were evaluated and compared. Generally, comparison of different cooling approaches revealed that the systems in which cooling is directly transmitted into the extraction phase, and/or cooling zone has adequate distance from the heating zone, are the most effective methods to increase the extraction efficiency, especially for the analysis of complicated solid matrices.

© 2016 Elsevier B.V. All rights reserved.

Contents

1. Introduction	54
2. Cooling-assisted solid-phase microextraction (SPME)	55
2.1. Cold-fiber SPME using liquid CO ₂	55
2.2. Cold-fiber SPME based on thermoelectric cooler	56
2.3. Cold-fiber SPME using circulating cooled fluids	58
2.4. Thin film microextraction (TFME) using cooled membrane	59
3. Cooling-assisted liquid-phase microextraction (LPME)	59
3.1. LPME with thermoelectric cooling of extraction phase	59
3.2. LPME reinforced by circulating cooled fluids	59
3.3. Gas purge microsyringe extraction (GP-MSE) with cooling systems	62
4. Miscellaneous applications of cooling systems in analytical extraction	62
5. Concluding remarks and future trends	63
Acknowledgements	63
References	63

1. Introduction

Solid-phase extraction (SPE) was introduced as an effective alternative to compensate limitations of the classical extraction methods such as liquid-liquid extraction (LLE) and Soxhlet [1]. Like any other scientific advances, after a while, scientists thought to rectify the defects of SPE using optical fibers, for sample extraction, and its direct introduction into GC injector followed by laser desorption [2]. This method reduced using of organic solvents, but

needed intricate instrumental reform of the GC system. The result of a clever idea for solving this problem was the implementation of a coated fused silica fiber on plunger's tip of a microsyringe followed by its introduction into the GC injector for thermal desorption [3]. In this way, solid-phase microextraction (SPME) was introduced by Pawliszyn. SPME reduced the steps and time of analytical analyses and opened up a new horizon for analysts.

More than two decades since SPME [4] was introduced, many efforts have been made to improve its modes [5] and applications [6]. However, due to complications with its practical manipulation, limited research has focused on improving the performance of the basic primary modes of SPME [7]. However, the proposed designs and developments not only were expensive and complicated, but

^{*} Corresponding author. Tel.: +98 663312061 12; Fax: +98 663312061 12.
E-mail address: a_ghiasvand@yahoo.com (A.R. Ghiasvand).

also could not significantly improve the abilities and extraction efficiency of SPME. Consequently, liquid-phase microextraction (LPME) procedure was introduced [8] and followed by publication of extensive research for its development [9,10], just like SPME. One of the few succeeded endeavors made to raise the efficiency of SPME was cold-fiber solid-phase microextraction (CF-SPME) [7]. This system can simultaneously provide heating sample matrix and cooling fiber coating. CF-SPME is very efficient in complicated matrices such as soil, sludge and clay, with analytes tightly attached to their active sites.

On the other hand, a serious challenge in environmental, biological and nutritional solid matrices is trapping and extracting volatile compounds. Direct thermal desorption (DTD) [11], static head-space coupled to gas chromatography (SHS-GC) [12], head-space sorptive extraction (HSSE) [13], and head-space solid-phase microextraction (HS-SPME) [14] are some general alternatives to conventional extraction methods. However, different variables including matrix complexity, physicochemical characteristics and amount of analytes in the sample should be considered to select the proper method [15]. HS-SPME is not as sensitive as DTD, but has a better sensitivity than SHS. Thus, for effective extraction of volatiles from solid matrices, improving the sensitivity of HS-SPME is a major concern [16,17]. The main challenges in HS-SPME are releasing low volatile analytes from their native matrix into headspace and collecting them onto microextraction phase, especially in complicated solid matrices. The most effective solution to release analytes from their matrix is thermal desorption, which provides enough kinetic energy and reinforces molecules to escape from their matrix, enhances the mass transfer to pass through the matrix, and increases their concentration in headspace by increasing vapor pressure. However, due to exothermic character of absorption, increasing temperature of the sample can conversely decrease trapping the analytes onto fiber's coating. Indeed, temperature has a bilateral effect. It increases the extraction efficiency by increasing concentration in headspace, but decreases the tendency of the coating to absorb the analytes. Therefore, in temperature profile of the headspace SPME sampling, there are usually an ascending part and a descending region, with an optimum temperature between them [18]. This optimal temperature is not usually high enough for significant improvement in extraction efficiency of volatiles, especially in solid matrices with their analytes firmly attached. This effect may be compensated by creating a temperature gap between fiber's coating and headspace, to simultaneously increase distribution coefficients of equilibriums between sample matrix and headspace as well as between headspace and fiber coating. Practically, this means heating sample matrix to high temperatures and concurrently cooling extraction phase at low temperatures. This strategy lets contaminated samples, such as soils and sediments, to be directly analyzed with minimal manipulation and in a single step.

In this review study, all cooling-assisted extraction approaches which are reported to date, are briefly described and classified based on techniques, as a monothetic classification system. Different important aspects of the CA-ME systems, such as fabrication techniques, cooling procedures, applications, and cooling performances are discussed and compared. Additionally, the efficiency of different cooling systems such as thermoelectric coolers (TECs) and cryogenic coolers (e.g., recirculating fluids) are discussed. Finally, according to the results of this study, some proper suggestions are offered for further extension and improvement of these methods.

2. Cooling-assisted solid-phase microextraction (SPME)

2.1. Cold-fiber SPME using liquid CO₂

The first promotion in SPME efficiency was made by introducing internally-cooled solid-phase microextraction (IC-SPME) device

by Zhang et al. in 1995 [7]. The IC-SPME device was successfully evaluated for the quantitative extraction of benzene, toluene, ethylbenzene, and xylene (BTEX) in clay soil samples. It used a Hamilton 1710RN gastight syringe barrel as the SPME device with discarding the plunger and needle and replacing by a 17-gauge needle. Moreover, a silica capillary tube was used as fiber and a piece of polydimethylsiloxane (PDMS) liquid polymer tubing as fiber's coating. Other type of coatings such as PA and DVB didn't have this type of tubing and can't be coated on this large bore tubing. Therefore, this type of SPME device was bound to PDMS, as the only possible sorbent. A silica capillary was used to deliver liquid carbon dioxide into the plunger to cool the fiber. This tube was fragile and hard to use. Additionally, it was bound to a predetermined and non-adjustable flow rate induced by its internal diameter, namely there was not an under-control restrictor to precisely fix the extractant's temperature, by controlling the flow rate of coolant liquid CO₂. The system was difficult to automate and limited to 250°C as maximum allowed temperature due to leakage probability. In general, using IC-SPME device was tedious. However, it was the starting point for improving the microextraction methods by cooling process.

The project remained inactive up to 2006 until a modified version of the previous design named cold-fiber headspace solid-phase microextraction (CF-HS-SPME) device [19] was introduced by Ghiasvand et al. (Fig. 1). In this new full-automated miniaturized design a piece of PDMS tubing was accommodated into an 18-gauge stainless steel needle, as the fiber's coating. This setup was robust and easy to use compared with the previously reported IC-SPME setup [7]. The CF-HS-SPME design used a 33-gauge stainless steel tubing to deliver liquid carbon dioxide for cooling the fiber. Moreover, a handmade restrictor was made and used for adjustable and precise control of flow rate and, consequently, control of coating's temperature at smaller intervals. Unlike the previous system, application of an adjusting tube prevented the fiber's coating to be stripped in contact with edges of a needle during movement inside it. In addition, using septum-cut and graphite ferrules with proper O-ring in Hamilton 1710RN gastight syringe barrel allowed applying temperatures above 250°C by ensuring no leaks in the system. The proposed CF-HS-SPME device was mounted on a CTC CombiPAL autosampler arm and full-automatically used. This system was successfully applied directly to extract and trap PAHs from sand and sediment samples, with minimal manipulation.

The CF-SPME device was coupled to GC-FID and GC-MS and applied for chemical screening of volatiles from tropical fruit samples [20]. It was coupled to a gas chromatography time-of-flight mass spectrometric detection (GC-TOF-MS) and directly applied to determine the flavor profile of fragrant rice samples [21]. The results showed that uncooked rice samples can be successfully analyzed even as dry kernels, without addition of water. It was also applied to determine chloroanisoles in cork samples [22]. In 2009, the CF-SPME device coupled to GC-FID was used to trap and analyze of nano-scale aerosols [23]. Furthermore, in 2009, the automated CF-SPME system was developed to study the desorption kinetics of PAHs from different laboratory-spiked samples and naturally contaminated sediments [24]. In another research, PDMS as a proper photoreaction medium and CF-SPME device as a convenient tool to perform UV exposure and consequently sample introduction into GC, have enabled the monitoring of photodegradation of volatile analytes for the first time [25]. More evaluation of CF-SPME was continued in 2011 by introducing a new optimization procedure for gaseous phase sampling of PAHs and phthalic acid esters (PEs) as model analytes [26]. The CF-SPME was further evaluated by combination of direct (DI) and headspace (HS) modes of CF-SPME for determination of PAHs and PEs as model analytes in soil samples [27]. To increase the extraction of analytes, which were different in volatilities, the direct extraction mode was changed to the headspace in an individual analysis and, simultaneously, extraction

Download English Version:

<https://daneshyari.com/en/article/1247686>

Download Persian Version:

<https://daneshyari.com/article/1247686>

[Daneshyari.com](https://daneshyari.com)