Journal of Chromatography A, 1216 (2009) 6852–6857

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Sample introduction in gas chromatography using a coiled wire filament

Tai V. Truong[a], Aaron N. Nackos[b], Jacolin A. Murray[a], Jon A. Kimball[a], Jason E. Hawkes[a,1], Donald J. Harvey[c,2], H. Dennis Tolley[d], Richard A. Robison[c], Calvin H. Bartholomew[b], Milton L. Lee[a,*]

[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA
[b] Department of Chemical Engineering, Brigham Young University, Provo, UT 84602, USA
[c] Department of Microbiology and Molecular Biology, Brigham Young University, Provo, UT 84602, USA
[d] Department of Statistics, Brigham Young University, Provo, UT 84602, USA

ARTICLE INFO

Article history:
Received 9 June 2009
Received in revised form 1 August 2009
Accepted 10 August 2009
Available online 13 August 2009

Keywords:
Sample introduction
Gas chromatography
Solvent-less injection
Coiled wire filament
Solid phase micro-extraction
Bacillus endospores
Fatty acid methyl esters
Polycyclic aromatic hydrocarbons

ABSTRACT

A simple device for field sampling and concentration of analytes for subsequent introduction into an injection port for gas chromatographic (GC) analysis has been developed. It consists of a tiny, coiled platinum wire filament (CWF) that is attached to a retractable plunger wire, which fits inside a syringe needle housing. Sampling is accomplished by dipping the end of the CWF in a liquid sample, which is drawn into the wire coil by capillary action, and introducing it into the injection port either before or after allowing the solvent to evaporate. The CWF can be used with or without a nonvolatile chemical coating. A major advantage of this sampling device is that nonvolatile sample matrix components remain on the wire coil, reducing the required injection port and liner cleaning frequency and contamination of the head of the chromatographic column. The coil itself can be easily cleaned between analyses by rinsing and/or burning off residual material in a small flame. The sampling coil facilitates specifically designed chemical reactions in the injection port, such as thermochemolysis and methylation. Applications demonstrated in this work include: (1) direct introduction of samples with little or no pre-treatment, (2) simultaneous thermochemolysis and methylation of lipid-containing samples such as bacteria and bacterial endospores for analysis of biomarkers, and (3) solid phase micro-extraction (SPME) using temporary wire coatings. The CWF allowed for significant reduction in sample preparation time, in most cases to less than a few minutes. The peak shapes examined for polycyclic aromatic hydrocarbon analytes (PAHs) were significantly better (asymmetry factors <1.3) when using the CWF sampling technique compared to splitless and on-column injection techniques (asymmetry factors >1.3). Extraction efficiencies for SPME (especially for high boiling point components such as PAHs) improved by an average of 2.5 times when using the CWF compared to the performance of commercially available SPME fibers. Coiled wire filaments and GC injection port liners were used for more than 100 *Bacillus* endospore thermochemolysis methylation analyses without the need for cleaning or replacement.

1. Introduction

In addition to the well-known hypodermic syringe in which a liquid or gas is sampled via a plunger-in-needle device, several other syringe-based devices intended for sample introduction into a standard gas chromatograph (GC) have been reported. Hypodermic syringes have been used as a means to introduce solids [1,2] or condensed vapors [3,4], sometimes with the inclusion of derivatization reagents inside the needle [5]. Needles packed with quartz wool were used to trap particulate matter and desorb volatiles inside the GC inlet [6,7]. A syringe-like device holding a removable capillary tube was used to sample "dirty" samples that had adhered onto the inner surface of the capillary following low-temperature removal of the solvent [8]. A method for concentrating an analyte on the tip of a syringe needle while inside a GC inlet was recently patented [9].

Several versions of syringes with an extendable solid body housed within a septum-penetrating needle have been reported. Hollowed out plungers possessing a small side vent were developed for capillary uptake and carrier gas expulsion of a sample [10,11]. Other extendable bodies intended mostly for solid samples have included straight [12] or flattened and twisted [13,14] wires or plungers with grooves [15] as well as tubes with "tongues" [16,17],

* Corresponding author. Tel.: +1 801 422 2135; fax: +1 801 422 0157.
E-mail address: milton_lee@byu.edu (M.L. Lee).
[1] Current address: University of Utah School of Medicine, Salt Lake City, UT, USA.
[2] Current address: Case Western Reserve University School of Medicine, Cleveland, OH, USA.

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.08.022

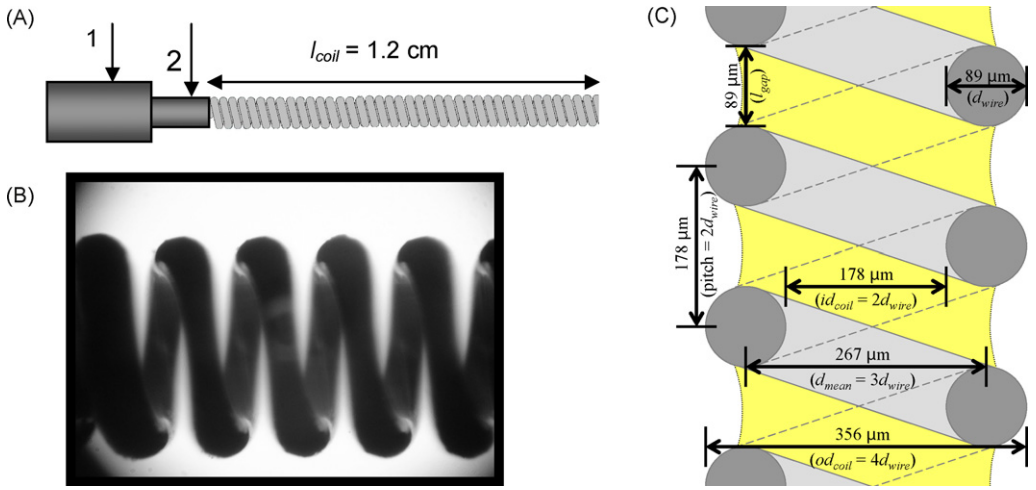

Fig. 1. (A) Schematic drawing of a coiled wire filament. The wire filament is held in place by a socket (2), which may be extended from or retracted inside an SPME needle (1). The coil diameter is 0.356 mm and the pitch is 0.178 ± 0.013 mm. (B) Photograph of an actual coiled wire filament produced by deflection coiling. (C) Cutaway schematic of the coil showing its dimensions.

needles with troughs [18], or needles with "windows" [19]. Sorbent materials have been installed on the inside of capillary tubes or on fibers or hollow bodies that can be extended from within syringe needles [20–22], including helical-shaped metal wires extendable from within a syringe [23–26].

In this paper, a new syringe-type sampling probe in the form of a coiled wire filament (CWF) is described. The CWF was designed for flexibility in GC sample introduction, allowing injection of both liquid and solid (i.e., solvent-less) samples, solid phase microextraction (SPME), and reaction-facilitated volatilization inside the heated injection port. Various types of samples ranging in complexity were analyzed and simultaneous thermochemolysis and methylation for differentiation of bacterial endospores was explored. Additionally, the ease with which this device performs SPME is demonstrated using temporary coatings of polymeric materials. Because the CWF greatly expands the types of samples that may be analyzed directly by GC, it is a complement to SPME and other solid-probe-type sample introduction techniques.

2. Experimental

2.1. Chemicals, materials, and samples

HPLC grade methanol, dichloromethane, and *n*-hexane were obtained from EMD (San Diego, CA, USA). Tetramethylammonium hydroxide pentahydrate (TMAH, >97%) was purchased from Sigma–Aldrich (St. Louis, MO, USA). H_2SO_4 (98%) was from Mallinckrodt Chemical (Phillipsburg, NJ, USA). Polycyclic aromatic hydrocarbons (PAHs) were obtained from a variety of sources. Apiezon N was from Kurt J. Leoker (Gilbert, AZ, USA). Pt–Ir wire (90% Pt, 10% Ir, approximately 90 µm diameter) was obtained from California Fine Wire (Grover Beach, CA; www.calfinewire.com).

A solution of PAHs was prepared by dissolving naphthalene, 1-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, 2,3-dimethylnaphthalene, acenaphthene, fluorene, diphenylmethane, and anthracene in dichloromethane at concentrations between 10 and 50 ppm each. This sample was analyzed using CWF, conventional splitless, and cold on-column injection techniques for comparison.

Vegetative bacteria or endospores were produced in a biosafety level-3 facility located on the Brigham Young University campus. *Yersinia pestis* was grown on Columbia agar at 28 °C, *Francisella tularensis* was grown on enriched Mueller-Hinton agar at 37 °C, and endospores of *Bacillus thuringiensis* (BT) were grown in Leighton-Doi broth at 32 °C.

2.2. Coiled wire filaments

The 90 µm O.D. Pt–Ir wire was deflection coiled by Motion Dynamics (Fruitport, MI; http://www.motiondc.com). Pt–Ir was chosen because of its increased stiffness relative to platinum, which allowed for better control over the coiling process. This family of materials generally exhibits high strength and oxidation resistance [27]. The length of the coiled section was 1.2 cm, the coil outer diameter was approximately 360 µm, and the coil pitch was approximately 180 µm (Fig. 1). A 0.5-cm straight "nib" was left on one end of the coil so that it could be inserted inside the empty socket of a Supelco SPME assembly and mechanically held in place by compressing the socket against the nib with a DMC crimping tool (Orlando, FL; www.dmctools.com).

2.3. Sample introduction using the CWF

During sampling, a small volume (~0.65 µL) of the sample was withdrawn onto the coiled wire by dipping the coil at least partially into the sample. Capillary forces rapidly drew the sample into the CWF and prevented any loss during sample transfer to the injection port. After drying in air (~20 s), the coil was retracted inside the syringe, the syringe was inserted inside the GC injection port, and the coil was extended. Immediately, the GC program was begun and the coil was left inside the injection port for 60 s. The coil and needle were solvent- or flame-cleaned (e.g., with a butane lighter or Bunsen burner) prior to subsequent use.[3]

2.4. Thermochemolysis and methylation of bacteria and bacterial endospores

A 500-µL volume of methanolic H_2SO_4 (1%, v/v) was added to a cell/spore pellet as received from the microbiology laboratory (i.e., 10^8–10^{10} cells/spores, slightly wet from the residual rinse water that had been used to clean them). The mixture was allowed to react for approximately 1 min at room temperature. A 200-µL volume of the cell/spore mixture was combined with 40 µL of 2.0 M methanolic TMAH and 40 µL of internal standard (50 ppm chrysene

[3] The melting temperature of 90–10 Pt–Ir is approximately 1800 °C [28].