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THERMAL-ASSISTED CHEMICAL ETCHING OF CAPILLARY COLUMNS

FIELD OF THE APPLICATION

The present invention is a method for enlarging the bore size of capillary tubes at selected sections. The method specifically concerns fabrication of capillaries used in capillary electrophoresis, electrochromatography, and micro-HPLC. A direct application of this method is to extend the detection zone of electrophoresis capillaries for better detection sensitivity.

BACKGROUND OF THE INVENTION

Capillary electrophoresis is an analytical technique whereby small volumes of mixed sample solution are separated in a narrow bore capillary tube filled with an electrolyte when an electric field is imposed across the capillary. Tile separation is based on differences in electric charges and molecular sizes of individual sample components. The principal components of a capillary electrophoresis system are a high-voltage power supply, a sample induction system, and a capillary that passes through the optical centre of a detection system connected to a data acquisition device.

In the most common case in capillary electrophoresis, the detection zone consists of a section of the capillary made transparent by removal of polyimide coating. In the detection system, a light source and a light sensor are placed outside the detection zone of the capillary. As the sample, so separated, migrates through the detection zone, light is passed along an optical path across the sample. By detecting the light output, information about the nature of the sample such as the chemical composition can be obtained.

Modern capillary electrophoresis systems use capillaries with an inner diameter of 25 -100 μm. Thinner capillaries promise a more efficient separation and a reduced analysis time. On the other hand, the narrow bore of capillaries severely limits the optical path length across the detection zone and the detection sensitivity since absorbance is proportional to optical path length. Although the optical path length can be increased by using capillaries with wider inner diameter, the separation efficiency of the capillary will drop considerably if the inner diameter of capillary is above 100 μm due to the increased current and associated Joule heating. One of the alternative approaches for extending the optical path length is to increase the inner diameter of the capillary locally in the detection zone, while maintaining a smaller internal diameter for other portion of the capillary. These capillaries have a "'bubble" in the flow path at the detection zone which provides an increased optical path length. By this way, the detection sensitivity can be increased several times without reducing the separation efficiency. A typical example may be seen in U.S. patent specifications number 5,061361 (Gordon).

Currently, two methods for fabricating capillaries with extended detection zone are available: one is blowing the selected section of a capillary which has been softened by imposing a high temperature, as described in U.S. patent 5,061,361, the other method is drawing a large ingot into a desired dimension following the procedures substantially the same as those employed to manufacture conventional fused silica capillaries [See U.S. patent 5,324,413. (Gordon)]. The first method requires a specifically designed lathe and operators with glass-blowing skills, whereas the second method requires equipment and techniques for manufacturing conventional fused silica capillaries.

OBJECT OF THE INVENTION

It is a primary object of the invention to provide a simple method for enlarging the detection zone of capillaries locally so that the detection sensitivity for capillary

electrophoresis can be improved. It is another object of the invention to provide a method for selectively enlarging the bore size of predefined sections of a capillary without changing the inner diameter of other portions of the capillary.

SUMMARY OF THE INVENTION

The present invention provides a simple method for selectively enlarging the bore size of capillaries at predefined positions. The method is based on chemical etching with hydrofluoric acid or other etching substances such as sodium hydroxide. The selective etching on a predefined position of a capillary is achieved by allowing etching solution to flow through the inner bore of the capillary while maintain the temperature at the predefined position sufficiently higher than at other portion of the capillary. Since the etching reaction at the predefined position is much faster than at other portion of the capillary, the bore at the predefined position can be extended to desired size before significant etching at other portions of the capillary has occurred. The method is applicable to capillaries used in capillary electrophoresis, electrochromatography,, and micro-HPLC. A direct application of this invention is to extend the detection zone of electrophoresis capillaries for improving the detection sensitivity.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 describes the set up for selectively enlarging the bore size of a capillary at a predefined position.

FIG.2 is a plan view of a resultant capillary with an enlarged detection zone.

FIG.3 are electropherograms of three carbamate pesticides separated by capillary electrophoresis.

DESCRIPTION OF THE EMBODIMENTS OF THE INVENTION

FIG. 1 shows a set up for selectively enlarging the bore size of a capillary at a predefined position. One end of capillary **1** is immersed m etching solution **2** contained in container **3**. Heating element **4** is placed around the predefined section **5** of capillary **1**. After Predefined section **5** has been heated to desired temperature (normally 3.5 times higher dm other portions of the capillary) etching solution **2** is forced to flow through the inner bore of capillary I either by imposing a pressure on the top of etching solution **2** or by creating a vacuum at end 6 of capillary **1**. After the etching has completed, capillary **1** is removed from etching solution **2** and heating element **4** and the inner bore of the capillary is washed with water. The etching process normally lasts less than 10 minutes.

FIG. 2 is a plan view of a resultant capillary with an extended detection zone. Detection zone **9** can be extended until its maximum inner diameter is almost equal to the outer diameter of capillary **7**. The dimension of detection zone **9** can be controlled by manipulating the etching time, etching temperature and the heating area. The effect of etching solution on the size of inner bore **8** of other portions of capillary **7** is negligible when the temperature at the detection zone is sufficiently higher dm at other portions of the capillary.

FIG. 3 gives a comparison on the detection sensitivity of carbamate pesticides metolarb **12**, propoxur **13**, and carbofuran **14**. Electropherogram **10** was obtained with an extended detection zone shown in Fig. 2. The electrophoresis conditions for electropherogram **11** was the same as for **10** except that the detection zone was not extended. FIG. 3 shows the use of an extended detection zone increased the peak height of the analytes 2-3 times without increasing the baseline noise.

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CLAIMS

1. A method for producing capillary zone cells for use in capillary electrophoresis, electrochromatography, and / or micro-HPLC by selectively enlarging the bore size of capillaries at predetermined sections comprising: allowing etching solution to flow through the inner bore of said capillary while maintaining the temperature at the section to be enlarged higher than at other portions of said capillary.

2. The method of claim 1 wherein the capillaries are made of fused silica or other glass materials and the etching solution may be hydrofluoric acid or other substances having etching effect on the material from which said capillaries are made.

3. The method of claim 1 wherein the capillary may be 1 to 150 μM in inner diameter and 180 to I000 μm in outer diameter before heating and etching.

4. The method of claim 1 wherein the inner diameter of the capillary is increased from its original size to a maximum size of no more than its original outer diameter.

5. A capillary zone detection cell system for use in capillary electrophoresis, electrochromatography and / or micro - HPLC produced by the method as in claim 1.