研究快报

A JOINT USED TO COUPLE HIGH PERFORMANCE CAPILLARY ELECTROPHORESIS WITH ELECTROCHEMICAL DETECTOR*

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1 Introduction

The major problem encountered when attempting to couple capillary zone electrophoresis (CZE) or micellar electrokinetic capillary chromatography (MECC) with electrochemical detection concerns the isolation of the detector from the large separation potentials applied. Failure to electrically isolate the detector leads to extremely high noise levels which can be several orders of magnitude greater than the Faradaic currents measured[1]. Wallingford Ewing[2,3] accomplished this isolation by incorporating an electrically conductive joint composed of porous Vycor glass near one end of the capillary. Huang and Zare[1] described a design of a simple and on-column frit that can fulfil the need to complete the electrical circuit prior to the outlet of the capillary and allows the use of electrochemical detection. Yik et al.[5] used graphite tube to connect separation and detection capillary with satisfactory results. O'Shea and co-workers[6] described a method for achieving the same objectives as those of the porous glass junction. They presented the use of Nafion tube that can fulfil the need of isolating the two segments in a capillary column.

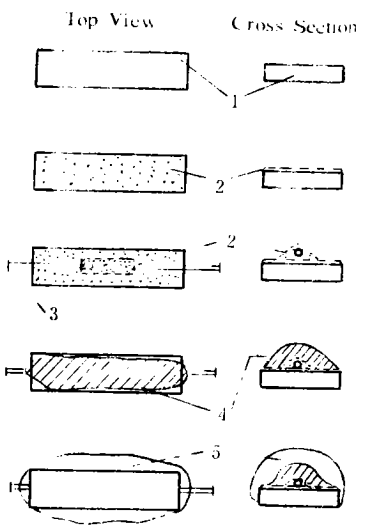

Fig. 1 Construction steps for preparing electrically conductive joint from Nafion solution
1. sintered ceramic, 2. Nafion layer, 3. capillary, 4. adhesive, 5. wax.

From above, the joints can be divided into two types, "tubular" and "on-column frit". Additional volume to separation and detection system can't be avoided in the tubular joint. The preparation method of the frit was very difficult for a general laboratory. Here we describe a method of preparing the joint from Nafion solution. The joint belongs to "on-column frit", but the preparation method is easy to master.

2 Experimental Section

Preparation of joint from Nafion Solution. A detailed preparation method of the joint is shown in Figure 1. The fused silica capillary is cut to required length. The surface of the capillary is lightly scored near the

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point approximately 2cm from the end with a tip. Gentle pressure applied to the scored region causes the column to break cleanly, leaving a joint that was easily reformed. The scored region is laid on a piece of sintered ceramic plate (1cm × 0.5cm × 0.2cm). The Nafion solution (per fluorinated ion-exchange powder, 5 Wt% solution in mixture of lower aliphatic alcohols and 1% water, Aldrich Chemical Copany, Inc. Milwaukee Wis. 53233 USA) is driped on the scored region again and again to form a Nafion film. CH3 adhesive (Ganxi Chemicals Factory, Jiangxi) is placed on the Nafion film. Liquid paraffin wax is used to protect the adhesive ageing. After the adhesive is cured, the assembly is placed into a plastic container in which there is a negative electrode.

Electrochemical Detection. A home-made high performance capillary electrophoresis (HPCE) system was used to test the Nafion film joint[7]. Electrochemical detection was performed with 5μm diameter carbon fibers protruding 1.0mm from drawn glass capillaries as the working electrodes. Samples were introduced by electroosmosis. The detection potential of the working electrode was controlled by 901-pA analyzer (Ningde Factory of Analytical Instruments, Fujian).

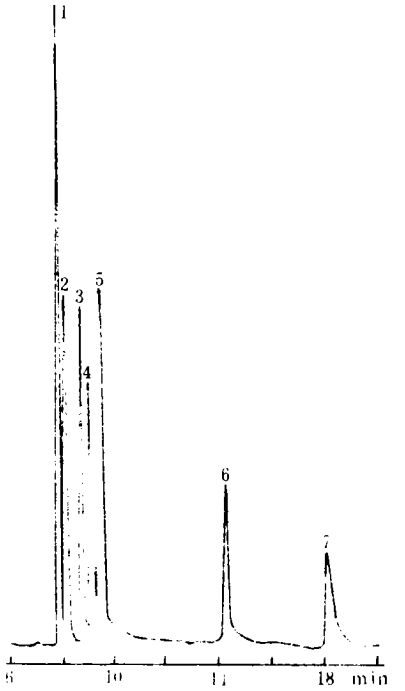

Fig. 2 MECC separation of seven phenols
Capillary, 65cm × 50μm (i.d.) fused silica capillary. Injection, 5s at 1kV. Peaks: 1. hydroquinone (1×10^{-1} mol/L), 2. trihydroxybenzene (2.3×10^{-1} mol/L), 3. pyrocatechol (2×10^{-1} mol/L), 4. phenol (1.0×10^{-1} mol/L), 5. methoxyphenol (1×10^{-1} mol/L), 6. chlorophenol (2×10^{-1} mol/L), 7. *p* bromophenol (2×10^{-1} mol/L).

3 Results and Discussion

Characterization of Capillaries with Nafion Film Joint. It is necessary to ascertain that the joint sturcture does not adversely affect the operaton of the capillary. CZE separations were run for a joint-free capillary and for a joint capillary of same length. It was found that the value of the current was about the same in both capillaries for the same applied electric field strength and buffer. As a further check, the electroosmotic flow was tested. The grounding was made either through the joint structure or through the capillary outlet, which is about 2 cm from the joint structure. It was observed that the electroosmotic flow rate was essentially the same within a single capillary.

These results encourage us to believe that the joint is a useful means for separating the capillary column into two segments, the one in which electrokinetic separation takes place, and the another in which the sample may be detected or collected without an external electric field being applied.

MECC separation with electrochemical detection. Figure 2 shows an electropherogram of a mixture of seven phenols obtained with the coupled MECC system (5mmol/L NH_3-NH_4Cl, 50mmol/L sodium dodecyl sulfate) and electrochemical detection at 465mV (vs. SCE). The excellent separatoin efficiency obtained with this system is evident in the hydroquinone peak which exhibits approximately 110 000 theoretical plates based on the half width.

Key words high performance capillary electrophoresis, electrochemical detection, joint, phenol mixture

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一种用于高效毛细管电泳电化学检测的接口

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摘要 在高效毛细管电泳分离和电化学检测时,遇到的一个突出问题是在对分离毛细管施加高直流电压的同时,有效地隔离高压电场对检测系统的干扰,但不给系统引入附加体积,即需使用一满足上述要求的接口来联接分离与检测毛细管。

Wallingfrod 和 Ewing[2,3]使用多孔玻璃管式接口,排除了两电化学系统间的相互干扰。Huang 和 Zare[4]描述了一种柱上烧结玻璃接口的制作方法。Yik 等[5]以石墨管完成了这种联接。O'Shea 等[6]以 Nafion 管来联接分离与检测毛细管得到满意的结果。

由此可见,就目前研究来看,该接口可分为两类:一类为"管式",另一类即为"柱上烧结"式。前者不可避免地会使毛细管较不使用接口的完整一根毛细管产生"附加体积";后者制作工艺复杂,一般实验室难以完成。

本文较详细地描述了以 Nafion 溶液制备 Nafion 膜接口的制作方法,其属"柱上烧结"式,可将两毛细管联结的像一根一样,不引入任何附加体积,对电渗流速的测定证实了这一点,即不论使用该接口与否流速均相同。在5mmol/L NH_3-NH_4Cl 和50mmol/L 十二烷基硫酸钠体系中对七种有机酚混合物(包括对苯二酚、邻苯三酚、邻苯二酚、苯酚、对甲氧基苯酚、邻氯酚和对溴酚)的胶束电动毛细管色谱分离和自制电化学检测器检测,获得了对对苯二酚110 000块理论板的分离效率,充分说明了该 Nafion 膜接口的性能良好,且该接口制作工艺易掌握,适于一般实验室的制作与使用。

关键词 高效毛细管电泳,电化学检测,接口,酚类混合物

向本刊投稿注意事项(二)

1994年《色谱》第4期284页上已刊载了"向本刊投稿注意事项(一)",现在主要谈一般学术会议论文集录用的文稿作者再向公开出版的学术刊物投稿时应注意的事项。现在一些学术会议仍只出版会议用论文集(无全国统一书号),因其属非正式出版物,所以该文集所录用的文稿作者仍可向国内外公开出版的学术刊物投稿。如今年4月在南京召开的"第十次全国色谱学术报告会"所出版的论文集录用的文稿,其作者仍可向本刊及有关刊物投稿。作者投本刊的应是论文全文而不是投会议的详细摘要稿(两者的投稿不应完全一样,否则公开发表此文就失去了原有的意义,简单地重复刊载实为一种浪费……)。本刊已在以前征文通知中要求作者在向会议投稿时事先有所安排。《色谱》编辑部在编辑出版"第十次全国色谱学术报告会论文集"过程中仍发现不少论文是全文而不是详细摘要,如该作者拟再向本刊投稿请勿将论文原样寄来,宜通过会议交流后再修改文稿使之完善、较之原稿有较大提高后,再投本刊。欢迎踊跃投稿,谢谢合作!

《色谱》编辑部
1995年3月