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科 技 查 新 报 告

**项目名称：****杯杂芳烃固相萃取材料用于黄酮类化合物的分离富集研究（宋体三号加粗）**

**委 托 人：河南中医药大学（单位名称）**

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中华人民共和国科学技术部

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| 查新项目名 称 | 中文：杯杂芳烃固相萃取材料用于黄酮类化合物的分离富集研究 |
| 英文：The preparation and application of heterocyclic calixarene sorbents in the extraction of flavonoids compounds**（仅查国内可省略）** |
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| **一．查新目的（项目名称要具体）**申报河南省科技进步奖 |
| **二．查新项目的科学技术要点 （宋体小四号）**此项目合成制备了杯杂芳烃化合物，并通过化学反应将之键合的硅胶表面，用于液相色谱固定相，以烷基苯、多环芳烃、苯酚、皂苷、核苷和阴离子为溶质，考察了该分离材料的分离性能；将杯杂芳烃键合到20μm硅胶表面，作为固相萃取材料，用于样品中黄酮类、蒽醌类化合物的分离和富集，取得了较好的实验效果。**（以委托书上的科学技术要点为基础，集中反映项目的主题，简明扼要说明项目概况、背景技术、拟解决或已解决的技术问题、拟采用或已采用的技术路线和方法、拟达到或已达到的目的、主要技术特征、技术指标、产品参数等）** |
| **三．查新点与查新要求****查新点：** 1.将杯杂芳烃化合物键合到硅胶表面，用于液相色谱固定相分离材料，考察了该分离材料的分离性能。2.将杯杂芳烃化合物键合到硅胶表面用做固相萃取材料，用于黄酮类化合物的分离和富集。**（要体现查新项目新颖性的技术创新点，表述要客观科学，条理清楚，简洁明了）****查新要求：**要求查找国内外与本课题相关的文献报道，并根据检索结果做出对比性结论。 |
| **四．文献检索范围及检索策略****（一）文献检索范围：**  **中文数据库**1.[中国学术期刊网络出版总库](http://epub.edu.cnki.net/grid2008/jump.aspx?url=http://acad.cnki.net/Kns55/loginid.aspx?uid=%7bUID%7d&p=Navigator.aspx?ID=CJFQ) 1994-2018.01（委托年月）2.[中国优秀硕士学位论文全文数据库](http://epub.edu.cnki.net/grid2008/jump.aspx?url=http://acad.cnki.net/Kns55/loginid.aspx?uid=%7bUID%7d&p=Navigator.aspx?ID=CMFD) 1999-2018.013.[中国博士学位论文全文数据库](http://epub.edu.cnki.net/grid2008/jump.aspx?url=http://acad.cnki.net/Kns55/loginid.aspx?uid=%7bUID%7d&p=Navigator.aspx?ID=CDFD) 1999-2018.014.[中国重要会议论文全文数据库](http://epub.edu.cnki.net/grid2008/jump.aspx?url=http://acad.cnki.net/Kns55/loginid.aspx?uid=%7bUID%7d&p=Navigator.aspx?ID=CPFD) 2000-2018.015.维普中文科技期刊全文数据库 1989-2018.016.万方数字化期刊 1990-2018.017.中国生物医学文献数据库 1978-2018.018.中国医药期刊文献数据库 1949-2018.019.中国知识产权局中国专利查询系统 1985-2018.0110.国家科技成果网（NAST） 1978-2018.01**外文数据库**1.SCIE（科学引文索引） 1997-2018.012.CPCI（会议论文引文索引） 1999-2018.013.EI（工程索引） 1969-2018.014.MEDLINE（美国医学文摘） 1965-2018.015.SciFinder（美国化学文摘） 1907-2018.016.PubMed 1965-2018.017.循证医学知识仓库 1990-2018.018.SPRINGER Journal 1997-2018.019.DIALOG- Allied and Complementary Medicine 1985-2018.0110.美国专利全文数据库（美国专利商标局） 1976-2018.01 **（说明：1、填写实际检索的数据库及其起止日期****2、从图书馆科技查新必检数据库中选择，10个左右****3、如果只查中文数据库，外文数据库不用体现）****（二）检索策略****检索词：**1、杯杂芳烃 Heterocyclic calixarene2、固定相 Stationary phase3、分离性能 Separation performance4、固相萃取 Solid extraction phase5、黄酮 Flavonoids**检索式：**1、杯杂芳烃 AND 固定相 AND 分离性能2、杯杂芳烃 AND 固相萃取 AND 黄酮1、Heterocyclic calixarene AND Stationary phase AND Separation performance2、Heterocyclic calixarene AND solid extraction phase AND flavonoids**（中外文分开撰写，书写要一端对齐，只查国内省略英文部分）** |
| **五．检索结果（相关文献一般提供十篇左右）**根据委托方提供的项目内容和检索要求，采用上述检索策略，经查**中国生物医学文献数据库、中国中医药信息网、**[**中国学术期刊网络出版总库**](http://epub.cnki.net/grid2008/jump.aspx?url=http://acad.cnki.net/Kns55/loginid.aspx?uid=%7bUID%7d&p=Navigator.aspx?ID=CJFQ)**、循证医学知识仓库、PubMed等（根据自己所查数据库调整）**，检出密切相关文献6篇，一般相关文献11篇，相关专利1项，未检出相关成果。**（一）密切相关文献（立项、开题无此部分）****1、胡锴,李睢,梁凯月,赵文杰,刘伟.采用二(四氧杂杯[2]芳烃[2]三嗪)固相萃取材料检测果汁中的芦丁[J].河南工业大学学报(自然科学版),2016,37(04):94-99.**摘要：通过化学反应,将二(四氧杂杯[2]芳烃[2]三嗪)键合到硅胶表面,制备了一种新型的固相萃取(solid-phase extraction,SPE)材料,并采用红外光谱仪和元素分析仪对合成的固相萃取材料进行了表征。结合高效液相色谱(HPLC),以芦丁为目标分析物对萃取性能进行了考察,结果表明这种新型的吸附剂可以提供多种分子间作用力,如π-π、疏水和氢键作用等。为了获得最优的固相萃取条件,对影响萃取效率的因素(如上样p H、速率,洗脱剂的种类、体积,淋洗液类型、体积等)进行了优化。在最优化的样品前处理条件下,建立分析方法,并用于果汁样品中芦丁含量的分离分析,结果表明在0.02~1.0μg/m L的范围内线性关系良好,方法的最低检测限是6.5 ng/m L,回收率在94.5%~98.2%之间,相对标准偏差<3.3%(n=5)。该方法对实际样品进行分析时,灵敏度高、测定结果准确,可用于果汁等样品中芦丁含量的分离分析。**（摘要如果太长，要适当修改，要完整。字体也要适当调整）****2、 K. Hu, S. Feng, M. Wu, S. Wang, W. Zhao, Q. Jiang, A. Yu, S. Zhang, Development of a V-shape bis(tetraoxacalix[2]arene [2] triazine) stationary phase for High performance liquid chromatography, Talanta, 2014，130，63-70**.Abstract：A new stationary phase for high-performance liquid chromatography was prepared by covalently bonding a V-shape cage heteroatom-bridged calixarene onto silica gel using 3-aminopropyltriethoxysilane as coupling reagent. The structure of the new material was characterized by infrared spectroscopy, elemental analysis and thermogravimetric analysis. Linear solvation energy relationship method was successfully employed to evaluate the new phase with a set of 34 solutes. The retention characteristic of the new phase shows significant similarities with ODS, as well as distinctive features. Multiple mechanisms including hydrophobic, hydrogen bonding, pi-pi and n-pi interaction are involved. The chromatographic behavior of the phase was illustrated by using alkylbenzenes, aromatics positional isomers and flavonoids as probes. Moreover, inorganic anions were individually separated in anion-exchange mode by using the same column. Thus, multi-interaction mechanisms and mixed-mode separation of the new phase can very likely guarantee its excellent chromatographic performance for the analysis of complex samples. The column has been successfully employed for the analysis of clenbuterol in animal urine, and it is demonstrated to be suitable and a competitive alternative analytical method for the determination of clenbuterol.**3、 Kai Hu, Wenfen Zhang, Huaixia Yang, Yongxia Cui, Jingya Zhang, Wenjie Zhao, Ajuan Yu, Shusheng Zhang. Calixarene ionic liquid modified silica gel: A novel stationary phase for mixed-mode chromatography. Talanta,2016, 152, 392-400**Abstract： A novel calixarene ionic liquid functionalized silica material was synthesized by the preparation of a new calixarene monomer and its grafting on mercaptopropyl modified silica gel. The material was characterized by infrared spectra, elemental analysis, and thermogravimetric analysis. To explore the retention mechanism of the stationary phase, linear solvation energy relationships (LSER) equation as an effective mathematical model was used. In addition to this, the distinct separation mechanisms were outlined by selected examples of chromatographic separations in the different modes. In reversed-phase liquid chromatography, this new stationary phase presented specific chromatographic performance when evaluated using alkylbenzenes, PAHs and phenols as solutes. Due to the existing polar functional groups, this stationary phase can also be used in hydrophilic interaction chromatography, six nucleosides and four ginsenosides were separated successfully in hydrophilic mode. Furthermore, anions can be separated on the column in anion exchange mode. Thus, this new material was can be applied as a new kind of mixed-mode stationary phase in liquid chromatography, which allows an exceptionally flexible adjustment of retention and selectivity by tuning the experimental conditions.**4、 K. Hu, Z. Deng, S. Li, M. Wu, W. Liu, S. Zhang, SPE-UHPLC-DAD Method for the Simultaneous Determination of Three Flavonoids in Grape Juice by Using Bis(tetraoxacalix 2 arene 2 triazine)-Modified Silica as Sorbent, Food Analytical Methods, 2017，10，3434-3442.**Abstract：In this study, bis(tetraoxacalix[2]arene[2]triazine) modified silica gel was successfully prepared and used as an efficient sorbent for solid-phase extraction. Coupled with ultra-high pressure liquid chromatography (UHPLC), the extraction performance of the sorbent was evaluated by using three flavonoids as model analytes. Main parameters, which affecting extraction efficiency were carefully optimized. The results showed that multiple intermolecular interactions were involved in the sample pretreatment procedure, including pi-pi, hydrophobic and hydrogen bonding interactions. Under the optimal conditions, the proposed method was applied for the analysis of three flavonoids in grape juice. Satisfactory linear ranges for flavonoids were obtained in the range of 5-200 ng mL(-1) for quercetin, 1-200 ng mL(-1) for luteolin, and 2-200 ng mL(-1) for kaempferol, with good correlation coefficients (> 0.9996). Limits of detection (LODs) were in the range of 0.5-2 ng mL(-1), and the LOQs were between 1 and 5 ng mL(-1). The recovery values of spiked grape juice ranged from 97 to 106% with relative standard deviations (RSDs) less than 4.7% (n = 3). This method exhibited the advantages of simplicity, rapidity, and low solvent consumption, and was promising for the separation and determination of flavonoids in grape juice and other matrixes.**5、 K. Hu, Z. Deng, B. Wang, Y. Cui, M. Miao, W. Liu, Q. Jiang, W. Zhao, Y. Huang, S. Zhang, Development of a decaaza-cyclophane stationary phase for high-performance liquid chromatography, Journal of Separation Science, 2015，38 ，60-66.**Abstract：A new stationary phase for high-performance liquid chromatography was prepared by covalently bonding a heteroatom-bridged cyclophane onto silica gel using 3-aminopropyltriethoxysilane as the coupling reagent. The structure of the new material was characterized by infrared spectroscopy, elemental analysis, and thermogravimetric analysis. The linear solvation energy relationship method was successfully employed to evaluate the new phase with a set of 25 solutes, and compared with octadecylsilyl and p-tert-butyl-calix[4]arene bonded stationary phases. The retention characteristics of the new phase are similar to the octadecylsilyl and conventional calixarene phases, and it also has distinctive features. In addition, the chromatographic behavior of the phase was illustrated by eluting alkylbenzenes and inorganic anions in the reversed-phase mode and anion-exchange mode, respectively. Thus, multi-interaction mechanisms and mixed-mode separation of the new phase can very likely guarantee its promising application in the analysis of complex samples. The column has been successfully employed for the analysis of triazines in milk, and it is demonstrated to be a competitive alternative analytical method for the determination of triazine herbicide residues.**6、 K. Hu, Y. Qiao, Z. Deng, M. Wu, W. Liu, SPE-UHPLC-FLD Method for the Simultaneous Determination of Five Anthraquinones in Human Urine Using Mixed-Mode Bis(tetraoxacalix 2 arene 2 triazine) Modified Silica as Sorbent, Journal of Analytical Methods in Chemistry, 2017，DOI 10.1155/2017/1963908.**Abstract：The five anthraquinones compounds (including aloe-emodin, emodin, physcion, chrysophanol, and rhein) are regarded as the main effective ingredients in rhubarb (Dahuang in Chinese, one of the commonly used Chinese herbal medicines). In this work, a simple and effective solid phase extraction (SPE) method based on bis(tetraoxacalix[2] arene[2] triazine) modified silica gel as adsorbent was developed. Coupled with UHPLC-FLD, the developed method was successfully applied for the measuring of main anthraquinones in human urine after oral administration of the extracts of rhubarb. To obtain the highest recoveries of the five anthraquinones in the SPE process, the main parameters which may affect extraction efficiency were optimized. The optimized sorbent amount, sample loading pH, sample loading rate, washing solution, and eluent condition were obtained. The developed method showed good linearity in 0.012-1.800 mu gmL(-1) for the five anthraquinones with correlation coefficients more than 0.9993. The investigated LOD values ranged from 3.9 to 5.7 ng mL(-1), while the LOQs were between 12.0 and 18.2 ng mL(-1). The recoveries of the method were also investigated, which were in the range of 94.8-106.6%. The application of the mixed-mode SPE materials in the proposed method was feasible and simple, and suitable for the enrichment of anthraquinones in urine samples.**（二）一般相关文献****1、顾薇薇. 杯芳烃咪唑盐衍生物的合成及功能化环三藜芦烃的研究[D].扬州大学,2011.**摘要：杯芳烃作为继环糊精、冠醚之后的第三代超分子主体化合物,对其进行各种功能化的修饰是近年来化学界的研究热点。通过对杯芳烃分子进行设计,引入各种功能基团,可以调节其空腔大小,增强其和金属的配位能力,提高其对分子、离子的识别能力等等。而一种新型的超分子主体化合物环三藜芦烃近年来也渐渐受到了广大的关注。环三藜芦烃具有与杯芳烃相似的物理和化学性质,人们对它也进行了各种功能化的衍生。本文以杯芳烃和环三藜芦烃为平台设计合成了各种多功能的衍生物,并对其进行了核磁共振、红外光谱及X-Ray衍射等表征,取得了一定的实验成果：1、以对叔丁基杯[4]芳烃和对叔丁基硫代杯[4]芳烃为原料,首先,K2CO3为碱和二溴烷烃反应制得对叔丁基杯[4]芳烃的双溴代烷基衍生物和对叔丁基硫代杯[4]芳烃全取代溴代烷基衍生物。其次,将溴代产物进一步与-甲基咪唑、N-丁基眯唑等反应,分别制得两种杯[4]芳烃的咪唑盐衍生物。进而将得到的配体再与金属进行配位,成功获得了几种配合物,并通过单晶X-Ray衍射确定了其结构。2、以四甲氧基间苯二酚杯芳烃母体为原料,在K2CO3作用下,和二卤代烷烃反应制得了全取代的溴代衍生物和氯代衍生物。将取得的溴代衍生物与-甲基眯唑、N-丁基咪唑反应制得相应的咪唑盐衍生物。本文对所有物质进行了红外光谱、核磁共振等表征,对部分物质进行了单晶X-Ray衍射检测。3、分别以邻甲氧基苯酚、邻苯二酚为原料,在路易斯酸催化下和三聚甲醛成环制得环三藜芦烃醚酯类衍生物,将该衍生物分别与水合肼、乙二胺、2-氨甲基吡啶等制得相应的酰肼、酰胺及芳环酰胺类衍生物,并将得到的肼解产品进一步与异氰酸苯酯、异硫氰酸苯酯反应。同时,从邻甲氧基苯酚出发合成了一种环三藜芦烃Schiff碱类衍生物。此外,本文还研究了具有水溶性的环三藜芦烃酰胺衍生物对金纳米粒子的保护作用,及其在水中的自组装情况。**2、阮耀宇. 新型芳基咪唑杯[4]芳烃衍生物的合成[D]. 齐齐哈尔大学, 2014.**摘要：本论文将芳基咪唑基团直接引入到杯芳烃的上、下沿，分别合成了上沿四芳基咪唑杯芳烃和下沿丁氧基三芳基咪唑杯芳烃衍生物，共17种未见文献报道的新型芳基咪唑杯[4]芳烃化合物。实验具体工作包括以下内容：上沿四芳基咪唑杯[4]芳烃衍生物的合成：首先合成两种重要的杯芳烃中间体——氨基杯[4]芳烃和醛基杯[4]芳烃，然后以一锅多组分偶联法分别合成得到四种上沿四芳基咪唑-1-取代的杯[4]芳烃衍生物和六种上沿四芳基咪唑-2-取代的杯[4]芳烃衍生物，并通过IR、1H NMR、13C NMR和MS等方法对以上10种未见文献报道的咪唑杯芳烃化合物进行了结构的表征，结果表明所合成的产物为目标化合物结构，并均采取的是杯芳烃的锥式构象。下沿三芳基咪唑杯[4]芳烃衍生物的合成：以对叔丁基杯[4]芳烃和1,4-二溴丁烷为原料，通过醚化反应合成得到下沿二溴丁氧基杯芳烃，再与一锅法合成得到的三芳基咪唑衍生物，在碳酸钾，N, N-二甲基甲酰胺和N2保护条件下，合成得到了七种下沿丁氧基三芳基咪唑杯[4]芳烃衍生物，并通过IR、1H NMR、13C NMR和MS等方法对以上7个未见文献报道的新化合物进行了结构的表征，结果表明所合成的产物为目标化合物结构，并均采取的是杯芳烃的锥式构象。与传统合成方法相比，基于杯芳烃结构单元的一锅多组分偶联法为上述目标产物的合成提供了一种操作简便，条件温和，具有较高选择性和原子利用率等优点的反应途径。**3、李宇飞,蒋宗林,彭琼,潘云芹.双咪唑鎓杯芳烃类似物的合成、结构表征及其对ATP的识别性能[J].西华师范大学学报(自然科学版),2015,36(01):36-40.**摘要：设计合成了两种具有水溶性的双咪唑鎓杯芳烃类似物3和4,经IR、1HNMR、MS谱确定了其结构.采用核磁滴定法,研究了主体化合物3、4对ATP的识别作用;结果表明,其结构更接近于杯芳烃的主体化合物3对ATP分子有显著的识别效果,而4对ATP分子的识别能力较弱.**4、赵冰,马明杰,阮耀宇,王丽艳,阚伟,宋波,石克炘.含氨基乙酸酯苯并咪唑杯[4]芳烃荧光分子探针的合成及光谱性能[J].化学试剂,2015,37(06):545-548.**摘要：以4-(N,N-二乙氧酰甲基)氨基苯甲醛和邻苯二胺为原料,首先得到了2-[4-N,N-二(乙氧酰甲基)氨基苯基]-1H-苯并咪唑。再将得到的苯并咪唑与5,11,17,23-四叔丁基-26,28-二羟基-25,27-二丁氧基杯[4]芳烃反应,合成了含氨基乙酸酯苯并咪唑杯[4]芳烃荧光分子探针L,并采用红外和核磁对所合成的化合物进行了结构表征和确认。通过紫外和荧光光谱实验研究表明,探针L在甲醇溶液中对Al3+具有选择性识别性能,且不受其他金属离子的干扰;当Al3+物质的量浓度增加到探针浓度的5倍时,探针L的荧光强度降低到最低值。Job’s曲线确定了探针与Al3+之间形成物质的量比为1∶1的金属配合物。**5、Yang F, Guo H, Jiao Z, et al. Calixarene ionic liquids: excellent phase transfer catalysts for nucleophilic substitution reaction in water[J]. Journal of the Iranian Chemical Society, 2012, 9(3): 327-332**Abstract：The first examples of calixarene ionic liquids 3 and 6 with 3D-shaped cavities were obtained in high yields by reacting calix[4] arene or thiacalix[4] arene with 1,6dibromohexane and then refluxing in 1-methylimidazole. The experiments of phase transfer catalysis in water suggested that they possessed excellentcatalytic properties of aromatic nucleophilic substitution reaction and benzyl nucleophilic substitution. The optimized yields of product in catalytic reactionwere as high as approximate 97% under mild reaction conditions. The cavities of calixarene skeleton played the crucial roles in catalysis and the stable cone conformation was favorable for catalysis.**6、**Hamdi A, Nam K C, Ryu B J, et al. Anion complexation. A ditriphenylphosphonium calix [4] arene derivative as a novel receptor for anions[J]. Tetrahedron letters, 2004, 45(24): 4689-4692.Abstract：A novel anionic receptor 2 consisting of a calix[4]arene bearing two alkytriphenylphosphonium has been prepared by two different procedures. The complexation occurred at the phosphonium sites probably due to electrostatic and/or pi-anion forces.**7、Tian M, Cheng R, Ye J, et al.** **Preparation and evaluation of ionic liquid-calixarene solid-phase microextraction fibres for the determination of triazines in fruit and vegetable samples[J]. Food chemistry, 2014, 145: 28-33.**Abstract：A new ionic liquid (IL)-calixarene coated solid-phase microextraction (SPME) fibre has been synthesized on the surface of quartz fibre by the sot-gel method.The coated fibre has been coupled with gas chromatography-flame ionisation detector (GC-FID) for the determination of triazines in fruit and vegetablesamples. The operation parameters including sample volume, extraction time, extraction temperature, desorption time, and sample pH have been investigated and optimised. Under the optimum conditions, the limits of detection of atrazine, simazine, ametryn, and cyanazine based on three times of standard deviations of blank by seven replications are 3.3, 4.4, 8.8, and 13.0 mu g kg(-1), respectively. The intra-day and inter-day relative standard deviations are less than 7.2% and 9.9%. The proposed method has been successfully applied to the determination of the four triazines in fruit and vegetable samples and theaccuracy is assessed through recovery experiments. **8、Pandey S, Ali M, Kamath G, et al.** **Binding of the ionic liquid cation 1-alkyl-3-methylimidazolium to p-tetranitrocalix [4] arene probed by fluorescent indicator displacement[J]. Analytical and bioanalytical chemistry, 2012, 403(8): 2361-2366.**Abstract：Acridine orange (AO) was used as a fluorescent probe molecule to study the encapsulation of an alkylimidazolium cation from a water-soluble ionic liquid (IL) within two cavitand species, p-tetranitrocalix[4]arene (1) and calix[4]resorcinarene (2), both in alkaline aqueous media. The addition of IL to the preformed [1·AO] adduct resulted in significantly increased fluorescence due to the expulsion of AO from the inclusion complex to the aqueous phase by competitive recognition of the 1-alkyl-3-methylimidazolium cation ([C(n)mim](+), n = 4 and 6) by 1. Conversely, the fluorescence signal dropped upon the addition of IL to the [2·AO] host-guest complex due to unfavorable binding between [C(n)mim](+) and 2. The formation of these postulated adducts is corroborated using ab initio calculations, which also provide evidence for the location of [bmim](+) at the lower external rim of [2·AO], providing an explanation for the observed luminescence quenching in the latter case. These results point to a number of different paths for exploration, ranging from the fluorescence monitoring of IL contamination in groundwater to the "daisy chaining" of macrocyles toward supramolecular ionic networks. They also broadly encourage the exploration of ILs in host-guest-based optical and mass spectrometric sensory systems.**9、 Shi J, Jia Q, Xu S.** **Characterization of calixarene/ionic liquid mixture as gas chromatographic stationary phase through thermodynamic parameters and LSER[J]. Chromatographia, 2012, 75(13-14): 779-787.****Abstract：**A mixture of 5,11,17,23-tetra-tert-butyl-25,26,27,28- tetraethoxycarbonyl methyloxy calix[4]arene (C[4]TECM) and 1-octyl-3-methylimidazolium tetrafluoroborate ionic liquid (OmI m+BF4−) has been employed as stationary phases in capillary gas chromatography. Its properties have been characterized through thermodynamic parameters and linear solvation energy relationship. The experimental results showed that C[4]TECM–OmI m+BF4− mixture as gas chromatographic stationary phase has high column efficiency and peak symmetry, which were evaluated using naphthalene and n-octanol, respectively. It was demonstrated that the interaction forces between the probe molecules and the stationary phase did not change over the entire temperature range studied due to an excellent linear relationship between lnk and 1/T, the retentions of the probe molecules on the C[4]TECM–OmI m+BF4− stationary phase are enthalpy-driven processes, and the interactions of the probe molecules with C[4]TECM–OmI m+BF4− stationary phase mainly include hydrogen bonding interaction, dipole–dipole interaction and dispersive interaction. However, the contribution of each interaction is in the order of A > L > S for the C[4]TECM–OmI m+BF4− stationary phase.**10、 Li X J, Ye C W, Huo X L, et al.** **Solid-phase microextraction using a diglycidyloxycalix [4] arene coated fiber combined with gas chromatography: very simple, rapid and sensitive method for the determination of chlorobenzenes in water[J]. Microchimica Acta, 2010, 168(1-2): 161-167.**Abstract: A fiber material for solid-phase microextraction (SPME) was obtained by blending 5,11,17,23-tetra-tert-butyl-25,27- dihydroxy-26,28-diglycidyloxycalix[4]arene with hydroxy-terminated silicone oil by sol-gel technology. It was used for headspace SPME combined with gas chromatography using electron capture detection to determine seven chlorobenzenes in water matrix. Optimum extraction conditions were 15 min at 20 °C with a solution containing 300 g L⁻¹ sodium chloride. The fiber exhibits far higher extraction efficiency than the commercially available poly(dimethylsiloxane) (PDMS) and PDMS-divinylbenzene fibers. The detection limits range from 0.32 to 2.25 ng L⁻¹, and the relative standard deviations are <5%. The calibration curves display a high level of linearity, with correlation coefficients ranging between 0.9996 and 1. The method was applied to analyze a lake water sample that was found to be polluted with 1,2,3,4-tetrachlorobenzene and hexachlorobenzene. It was compared to the United States Environmental Protection Agency method and other recently introduced methods. The results demonstrate that the technique is rapid, simple, and sensitive, and thus represents an attractive alternative for ultra-trace analysis of chlorobenzenes in water samples.**11、Deng Z, Hu K, Zhang Y, et al.** **On-cartridge derivatisation using a calixarene solid-phase extraction sorbent for facile, sensitive and fast determination of formaldehyde in beer[J]. Food Chemistry, 2016, 211: 314-319.**Abstract：This work demonstrates the successful application of an on-cartridge derivatisation procedure for facile, fast and sensitive determination of formaldehyde in beer by HPLC-UV. The derivatisation and solid-phase extraction (SPE) were integrated into a novel calixarene SPE sorbent: tetraazacalix[2]arene[2]triazine bonded silica gel. Specifically, 2,4-dinitrophenylhydrazine was adsorbed onto the sorbent in advance, based on the charge-transfer interaction between the macrocyclic molecule and nitrobenzenes. The method was optimised and validated: under the optimal conditions of derivatisation, SPE and HPLC separation, good linearity was obtained in the range of 0.080-3.2μgmL(-1) with a correlation coefficient of 0.9939, the limit of detection was 3.0ngmL(-1) (S/N=3), the limit of quantification was 10ngmL(-1) (S/N=10), and the recovery level using this method was desirable at 75-84%. The developed method was successfully applied to determine formaldehyde content in real beer samples; the results were in the range of 0.11-1.1μgmL(-1).**（参考文献在每一个类目下按照先中文文献后英文文献的顺序罗列）****（三）相关专利****1、胡锴,吴明侠,陈志红,崔永霞,龚海燕. 咪唑杯[4]芳烃键合硅胶固定相及其制备方法应用[P]. 授权号：201510953744X. 河南：CN105536749A, 2016-05-04.**摘要：本发明涉及咪唑杯[4]芳烃键合硅胶固定相及其制备方法与应用,可有效解决咪唑杯[4]芳烃键合硅胶固定相的制备与应用问题,方法是,将咪唑杯[4]芳烃1g与巯丙基三乙氧基硅烷化硅胶3-4g加入乙腈溶剂50-60ml中,再加入催化剂偶氮二异丁腈0.1g,氮气保护下,在催化剂的催化下55-65℃反应20-24h,过滤,依次用甲苯、甲醇、水和丙酮各洗涤一次,60-70℃下真空干燥10-12h,即得；所述的咪唑杯[4]芳烃键合硅胶固定相在液相色谱分离有机化合物中的应用。本发明制备方法简单,易操作,成本低,有效用于液相色谱分离有机化合物,易于工业化生产,经济和社会效益巨大。**（四）相关成果**未检出 |
| **六．查新结论** 综合文献分析：在查到的国内相关文献中，胡锴等采用制备的二(四氧杂杯[2]芳烃[2]三嗪)固相萃取材料对果汁中的芦丁进行了分离富集，效果良好。（参见密切相关文献1）。顾微微以对叔丁基杯[4]芳烃和对叔丁基硫代杯[4]芳烃为原料,将其溴代产物进一步与-甲基咪唑、N-丁基眯唑等反应,分别制得两种杯[4]芳烃的咪唑盐衍生物。进而将得到的配体再与金属进行配位,成功获得了几种配合物,并通过单晶X-Ray衍射确定了其结构。（参见一般相关文献1）。阮耀宇等将芳基咪唑基团直接引入到杯芳烃的上、下沿，分别合成了上沿四芳基咪唑杯芳烃和下沿丁氧基三芳基咪唑杯芳烃衍生物，共17种未见文献报道的新型芳基咪唑杯[4]芳烃化合物。（参见一般相关文献2）。李宇飞等设计合成了两种具有水溶性的双咪唑鎓杯芳烃类似物，经IＲ、1HNMＲ、MS 谱确定了其结构．采用核磁滴定法，研究了它们对ATP的识别作用。（参见一般相关文献3）。赵冰等合成了含氨基乙酸酯苯并咪唑杯[4]芳烃荧光分子探针，并采用红外和核磁对所合成的化合物进行了结构表征和确认。通过紫外和荧光光谱实验研究表明,探针在甲醇溶液中对Al3+具有选择性识别性能,且不受其他金属离子的干扰;当Al3+物质的量浓度增加到探针浓度的5倍时,探针L的荧光强度降低到最低值。Job’s曲线确定了探针与Al3+之间形成物质的量比为1∶1的金属配合物。（参见一般相关文献4）。在查到的国外相关文献中，Kai Hu等制备了二(四氧杂杯[2]芳烃[2]三嗪)液相色谱固定相分离材料，以烷基苯、多环芳烃、苯酚、皂苷、核苷和阴离子为溶质，考察了固定相的色谱性能，结果表明，在分离过程中存在π-π作用、氢键作用等多重作用力。（参见密切相关文献2）。Kai Hu等将杯芳烃离子液体键合到5μm硅胶表面，用于液相色谱固定相，以烷基苯、多环芳烃、苯酚、皂苷、核苷和阴离子为溶质，考察了固定相的色谱性能，结果表明固定相除了具有反相作用机理，还具有亲水作用和离子交换作用等混合分离模式。（参见密切相关文献3）。 Kai Hu等采用制备了二(四氧杂杯[2]芳烃[2]三嗪)固相萃取材料，并对葡萄汁中的三种黄酮类化合物进行了分离富集，效果良好。（参见密切相关文献4）。Kai Hu等制备了环蕃类杯芳烃固定相，并对分离性能进行了研究。（参见密切相关文献5）。Kai Hu等采用制备的二(四氧杂杯[2]芳烃[2]三嗪)固相萃取材料，并对尿液中的五种蒽醌类化合物进行了分离富集，效果良好。（参见密切相关文献6）。Yang F等设计合成的杯芳烃离子液体化合物，将之用于水相亲核取代反应的相转移催化剂。（参见一般相关文献5）。Hamdi A等合成了三苯基膦杯芳烃衍生物，考察了其与阴离子络合作用，成功将之用于阴离子识别传感器。（参见一般相关文献6）。Tian M通过溶胶凝胶法，将离子液体和杯芳烃涂覆在石英纤维表面合成固相微萃取纤维，结合气相色谱法检测水果和蔬菜样品中三嗪类农药残留。（参见一般相关文献7）。Pandey S采用吖啶橙作为荧光探针分子研究了烷基咪唑阳离子与两种杯芳烃的包结作用。（参见一般相关文献8）。Shi J将5,11,17,23-四-叔丁基-25,26,27,28-四乙氧基羰基甲氧基杯[4]芳烃和 1-辛基-3-甲基咪唑 四氟硼酸盐离子液体的混合物作为气相色谱毛细管电色谱固定相。采用热动力学参数和线性溶剂能方程，考察了它的色谱性能。（参见一般相关文献9）。Li X J将5,11,17,23-四叔丁基--25,27-二羟基-26,28-二环氧丙氧基杯[4]芳烃和端羟基杯芳烃混合涂覆到纤维表面，用做固相微萃取材料。结合顶空固相微萃取和气相色谱电子捕获技术测定水样中七种氯苯化合物。（参见一般相关文献10）。Deng Z采用杯芳烃固相萃取材料建立了一种柱上衍生技术，快速简便的测定了啤酒中的甲醛含量。（参见一般相关文献11）。相关专利中，胡锴等发明了咪唑杯[4]芳烃键合硅胶固定相及其制备方法与应用,可有效解决咪唑杯[4]芳烃键合硅胶固定相的制备与应用问题。（参见相关专利1）。**（综合文献分析，一定要把文摘综合一下，不要直接从上面的摘要粘贴下来）**综上所述：**（查新结论文字表述必须客观公正，不得有主观性语言，最好用这样的表述：****国内（外）公开发表的文献中，未见（已见）……报道****国内（外）公开发表的文献中，未有（已有）……报道****国内（外）公开发表的文献中，未检到（已检到）……报道）**1、国内外公开发表的密切相关文献中，已见本课题组成员关于将杯杂芳烃键合到硅胶表面，用于液相色谱固定相分离材料，研究其分离性能的报道；已见本课题组将杯杂芳烃键合到硅胶表面，用于固相萃取材料，富集净化黄酮、蒽醌等物质的报道。在一般相关文献中，已见将杯杂芳烃涂覆到纤维表面用做固相微萃取材料的报道，已见将二(四氧杂杯[2]芳烃[2]三嗪)固相萃取材料对尿液中的五种蒽醌类化合物进行分离富集的报道，未见将杯杂芳烃用做样品前处理材料，富集净化样品中的黄酮、蒽醌类物质的报道。**（至少列出两个“已见”的对比研究）**2、相关专利中，已见本课题组成员对咪唑杯[4]芳烃液相色谱分离材料的制备及相关应用的相关报道，未见其他相关专利。3、未检出相关成果。查新员： 查新员职称：馆员审核员： 审核员职称：副研究馆员 （科技查新专用章）年 月 日 |
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