

液相微萃取技术及其在食品分析中应用现状

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摘 要: 液相微萃取是一种绿色环保的样品前处理技术, 具有选择性好、操作简单、快速、富集倍数高、所需有机溶剂用量少等特点而成为一种备受关注的新型样品分离富集技术。近些年, 该技术已经在水样、土壤、饮品及食品等样品的分析中得到广泛应用。本文综述了液相微萃取技术近期的研究进展及其在食品安全分析领域的应用, 包括饮品、蔬菜水果、谷物及动物性组织等食品中农药、兽药、酚类物质、持久性污染物及其他一些物质的分析检测, 并对其发展趋势进行展望。

关键词: 液相微萃取; 样品前处理; 食品安全; 食品检测

Liquid-phase microextraction technique and its application on food analysis

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ABSTRACT: Liquid-phase microextraction (LPME) is an environmental benign separation and enrichment technique because of good selectivity, simple operation, rapidity, high enrichment factor, and low dosage of organic solvent and so on. At present, it has been widely applied in the analysis of environmental water samples, soil samples, beverages, foods and so on. This present review focused on the updated developments of LPME and its applications in food safety analysis, including the determination of different substances like pesticides, veterinary drugs, phenols, persistent organic pollutants and others in beverages, fruits and vegetables, cereals, animal tissue and other foods. Finally, its development trend was prospected.

KEY WORDS: liquid-phase microextraction; sample preparation; food safety; food analysis

1 引 言

近些年来食品安全问题层出不穷, 食品中农药残留、兽药残留、非法添加剂、重金属等有害物质等问题频频出现, 食品安全已成为全社会的广泛关注的热点。食品安全分析是保证食品安全的基础手段和方法, 如何快速、准确地分析检测食品中有毒有害物质已成为食品安全分析的关键点^[1]。样品前处理技术和分析检测技术是解决食品分析检测的两大关键问题。近年来, 现代仪器分析与检测技术的效率有大幅度提高, 特别是色谱、质谱等灵敏度高的检

测技术的出现, 很大程度上提高了分析的准确度和高效性。然而, 样品前处理技术的发展却远远落后于分析检测技术, 如何提高样品前处理效率已成为分析化学发展的关键环节和瓶颈问题。文献报道, 一般实验室中用于样品前处理的时间约占整个分析时间的 2/3, 而只有 10%的时间是用于仪器分析检测^[2]。另外, 分析样品种类多、组成复杂、物理形态广泛也对样品前处理提出越来越高的要求, 因此样品前处理技术面临着严峻挑战。探索快速、高效、简便、自动化率高的样品前处理新方法已成为分析化学的主要研究方向之一。

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2 微萃取技术研究概况

目前, 国内分析检测领域已经开发了一些基于新原理或传统技术改进基础上的样品前处理新技术, 如微萃取技术: 包括固相微萃取(solid-phase microextraction, SPME)及液相微萃取(liquid-phase microextraction, LPME)。

SPME 是在固相萃取(solid-phase extraction, SPE)技术基础上发展的一种新型样品前处理方法, 该方法集采样、萃取、浓缩、进样于一体。目前, SPME 在食品和环境领域中已经得到广泛应用, 如农药残留、兽药残留以及多氯联苯等污染物的检测^[3-5]。但是一些杂质在萃取纤维上吸附后难以清除, 这不仅会影响结果准确性, 还会影响纤维萃取针头寿命。对于基质复杂的样品, SPME 技术干扰比较大, 结果重复性差。

LPME 是 1996 年在液-液萃取(liquid-liquid extraction, LLE)基础上发展起来的一种新型样品前处理技术^[6,7]。LPME 具有灵敏度高、富集效果好、所需有机溶剂量及样品量少、操作时间短、重现性好、适用范围广等特点。相对于固相萃取、固相微萃取技术, LPME 还改善了吸附孔道易堵塞的缺点, 回收率高, 且实验装置携带方便^[8,9]。目前, LPME 技术已成为国内外样品前处理技术中的一个热点技术, 具有广阔的应用空间。LPME 目前已在环境、药品和食品等领域得到应用^[10-12]。

3 液相微萃取技术的萃取模式

根据目标物和样品基质的不同, 目前液相微萃取技术的萃取模式主要有单滴微萃取、分散液相微萃取和中空纤维膜液相微萃取 3 种萃取模式。

3.1 单滴微萃取(single drop microextraction, SDME)

单滴微萃取是液相微萃取中最简单的模式, 以微升数量级的液滴代替外覆纤维作为萃取剂, 通常悬挂于普通

色谱进样器的针头。SDME 主要原理是根据目标物在微量进样器尖端的萃取微滴和液体样品之间的分配原则, 待萃取完成后, 微滴被抽回至微量进样器, 注入高效液相色谱(high performance liquid chromatography, HPLC)等仪器后进行分析检测^[13]。目前, 根据萃取平衡时共存相的数目可以将单滴微萃取分为两相和三相单滴微萃取两类, 7 种萃取模式^[14](图 1)。

SDME 作为一种高效的样品前处理方法可以与多种仪器联用, 如原子吸收光谱(AAS)^[15]、气相色谱(GC)^[16]、紫外分光光度计(UV)^[17]、高效液相色谱(HPLC)^[18]和质谱(MS)^[19]等。虽然 SDME 具有有机溶剂用量少、富集倍数大、灵敏度高等优点, 但该技术需要较快的搅拌速度、较高的萃取温度和较长的萃取时间, 而且萃取的稳定性和灵敏度都不稳定, 因而在实际应用中收到了一些限制^[20]。另外, SDME 没有样品净化的功能, 只能用于干净的样品基质, 所以 SDME 的适用范围十分有限^[21]。

3.2 分散液相微萃取(dispersive liquid-liquid microextraction, DLLME)

分散液相微萃取是 Rezaee 等^[22]于 2006 年提出的一种新型液相微萃取技术, 类似于微型化的液-液萃取技术。DLLME 基本原理是先将混有微量萃取剂的分散剂注入样品溶液中, 萃取剂在分散剂作用下在样品溶液中形成分散的细小液滴, 形成萃取剂-分散剂-样品溶液三元乳浊液体系, 由于萃取剂和分析物的接触面积增大, 待测物在样品溶液及萃取剂之间快速达到分配平衡, 目标物被萃取富集而进行分析测定^[23]。

根据萃取剂类型以及萃取方式的不同, DLLME 分为离子液体分散液液微萃取(IL-DLLME)、悬浮固化分散液液微萃取(SFO-DLLME)、超声乳化分散液液微萃取等形式^[24]。DLLME 可以与多种仪器联用, 如气相色谱仪^[25,26]、液相色谱仪^[27,28]、原子吸收分光光度计^[29,30]等。

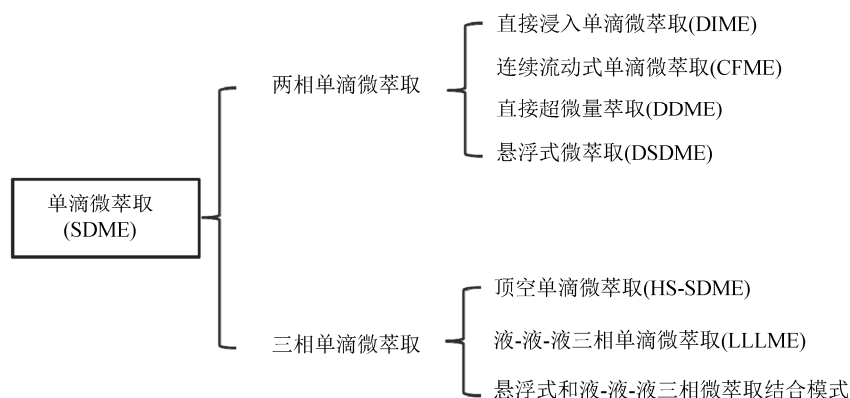


图 1 单滴微萃取萃取模式

Fig. 1 Models of single drop microextraction

与 SDME 和 HF-LPME 相比, DLLME 克服了 SDME 技术中悬挂的液滴不稳定、萃取难平衡、有机溶剂用量多的缺点,同时 DLLME 也避免了 HF-LPME 的萃取速率慢、效率低等缺点^[24]。DLLME 集采样、萃取和浓缩于一体,具有操作简单、快速、成本低、有机溶剂用量少、对环境友好、萃取时间短、富集效率高等特点,在农药残留、重金属等的痕量分析中具有广泛的应用前景^[31]。

3.3 中空纤维膜液相微萃取(hollow fiber-protected liquid phase microextraction, HF-LPME)

HF-LPME 是在 1999 年由 Pedersen-Bjergaard 和 Rasmussen 提出的一种新型液相微萃取技术^[32]。HP-LPME 的原理是 HF-LPME 以多孔性中空纤维膜作为有机溶剂载体,分析物先被由多孔纤维支撑的憎水的液膜层萃取,然后经液膜层进入纤维管内的萃取相中萃取,萃取液可直接进样分析。

中空纤维液相微萃取主要有 3 种模式:中空纤维膜液-液两相微萃取、中空纤维膜液-液-液三相微萃取(液相微萃取/反萃取)和动态中空纤维膜液相微萃取,其中动态中空纤维膜液相微萃取又分为动态两相微萃取和动态三相微萃取。HP-LPME 的这 3 种模式都具有集萃取、净化、浓缩为一体且操作简便的特点^[33]。目前,已经有很多 HF-LPME 与 GC^[34,35]、HPLC^[36,37]、CE^[38,39]联用的报道。HF-LPME 具有较高的回收率和富集倍数,由于大分子、颗粒杂质等不能进入纤维孔,因此, HF-LPME 样品净化能力突出。而且中空纤维是一次性使用的,不会引起交叉污染。HF-LPME 虽然萃取时间较长,但它可以同时平行展开实验,萃取工作效率较高,尤其适合于大批量样品的处理^[40]。因此, HF-LPME 在痕量分析领域具有广泛的应用前景。

4 液相微萃取技术的影响因素

4.1 有机溶剂的选择

有机溶剂的选择是提高液相微萃取效率的关键因素,应根据“相似相溶原理”来选择有机溶剂^[41]。有机溶剂的选择应遵循以下原则:对目标物有较强的溶解度和高选择性,三相体系中有有机溶剂对目标物的溶解度要适中;挥发性小且在样品溶液中不溶或溶解度低;与中空纤维膜有较好兼容性和亲和性;应有很好的色谱行为,易于与目标分子分离;尽可能选择毒性小、对环境危害小的有机溶剂。单滴液相微萃取常选用灵敏度更高的芳香族溶剂^[42]。分散液相微萃取常选用卤代烃为萃取剂,如卤苯、氯仿、四氯化碳等,分散剂常选用甲醇、乙醇、丙酮等^[43]。中空纤维液相微萃取常用的萃取溶剂有 1-辛醇、正己基醚、二己醚、甲苯、乙酸乙酯等^[44]。一般两相萃取系统多用于气相色谱,有机溶剂体积为 1 μL ;三相萃取中一般用于液相色谱和毛细管电泳,有机溶剂和受体相体积通常为 5~25 μL 。

4.2 萃取时间

因为液相微萃取需一定时间后才能达到分配平衡,而萃取量与萃取时间不成线性,若将到达分配平衡作为萃取终点的达到,不仅萃取时间过长,也不适合实际操作,而且也会对有机液滴大小产生影响,使萃取量下降。在实际操作中,为保证分析结果的重现性,通常选择接近平衡的时间为合适的萃取时间,萃取时间一般为 30~45 min。对于 DLLME 萃取模式,由于在溶液形成乳浊液之后萃取剂被均匀地分散在水相中,待测物可以迅速由水相转移到有机相并达到两相平衡,因此萃取时间对萃取效率没有显著影响^[43]。

4.3 萃取温度

温度升高,可以增加待测物向有机相的扩散系数,对流过程加强,缩短达到平衡的时间;但升温会减小待测物分子的分配系数,待测物在溶剂中的萃取量减少。另外,还可增加有机溶剂在样品溶液中的溶解度,加剧溶剂损失和挥发^[44]。因此,在具体实验操作时需要兼顾萃取时间和萃取效果两方面的因素,寻求最佳萃取温度。

4.4 盐效应

为减小萃取溶剂的水溶性,水相中经常会加入适量的 NaCl 等盐用以提高萃取效率^[45]。但随着盐浓度的增加,被测物进入液滴的扩散速度减小,萃取效率随之降低。但对于 HF-LPME 萃取模式,在样品溶液中加入盐对不同分析物萃取效率的影响各不相同,有的提高,有的无明显变化,有的甚至降低^[46,47]。另外无机盐还会增强目标物与盐之间的静电作用^[48]。所以,样品溶液中盐效应对萃取结果的影响要具体实验具体分析。

4.5 pH 的选择

对只适用于亲脂性高或中等的分析物的两相 LPME,分配系数的大小是决定回收率的关键因素。对亲水性较强的带电荷物质可利用三相萃取体系进行分离,给体相和受体相的 pH 值在三相萃取体系中对萃取结果的影响尤为重要^[49]。一般对弱碱性物质,样品溶液的 pH 应在碱性范围,接收相的 pH 值应在酸性范围。而对于酸性物质,样品溶液的 pH 应在酸性范围,接收相的 pH 值应在碱性范围。通常溶液的 pH 值要与被测物的 pKa 值要相差 2~3 个 pH 单位^[50]。

4.6 其他因素

HF-LPME 要选择适中的搅拌速率。搅拌可以增加目标分子在液相中的扩散系数,缩短萃取时间,提高萃取效率。但搅拌过快可能破坏萃取液滴,产生气泡粘附在中空纤维上,阻碍传质。对于动态 HF-LPME 还需优化微进样器塞的移动速度,停留时间和萃取循环次数等参数^[51]。

5 液相微萃取技术在食品分析中的应用

近年来食品安全事故频发, 食品安全问题日趋严重, 食品安全已成为全社会广泛关注的问题。食品分析是食品安全监控中的重要环节, 而食品样品基质复杂, 目标物在样品中含量通常非常低。如何从复杂的食品样品中成功实现对目标物的分离与富集, 已成为食品安全分析中的关键问题。LPME 是一种快速、准确、灵敏和费用低的样品预处理技术, 并能与 GC、HPLC 和 CE 等分析仪器联用。即使在处理复杂基质时, 该方法也能得到很好的富集倍数和净化效果。目前, 该技术已广泛地应用于食品样品中农药、

兽药及各种有毒有机化合物的检测中。

5.1 饮料中不同物质的分析测定

饮料基质相对简单, 目前 LPME 的 3 种萃取模式在饮料的农药残留、防腐剂、杀菌剂等各种污染物的检测都有报道。表 1 列举了 LPME 在饮料基质中不同物质的分析实例。

5.2 酒类样品中不同物质的分析测定

酒类样品也是 LPME 应用较多的样品类型, 在农药残留等方面已有多篇文献报道(表 2)。

表 1 LPME 在饮料样品中的应用
Table 1 Applications of LPME on beverage samples

目标物	样品基质	萃取模式	检测仪器	参考文献
有机磷农药	果汁	单滴微萃取直接/循环流动单滴微萃取	GC-FPDGC	[52] [53]
挥发性硫化物	啤酒饮料	顶空单滴微萃取, 直接单滴微萃取	GC-FPD	[54]
苯甲酸和山梨酸	饮料	三相中空纤维液相微萃取	UPLC-MS	[36]
有机酸	饮品	三相中空纤维液相微萃取	HPLC	[55]
杀菌剂	柑橘汁	中空纤维膜液相微萃取	LC-MS	[56]
三唑类杀菌剂	葡萄汁	中空纤维膜液相微萃取	GC-MS	[57]
抗氧化剂	果汁	中空纤维膜液相微萃取	HPLC	[58]
西维因、三唑磷	果汁	分散液相微萃取	GC-MS	[69]
农药	苹果汁	分散液相微萃取	GC/MS	[60]
拟除虫菊酯类农药	果汁	分散液相微萃取	GC-MS	[61]
柠檬酸	饮料	中空纤维膜液相微萃取	HPLC	[62]
		静态直接浸入法		
增塑剂	饮料	动态直接浸入法	GC	[63]
		中空纤维膜法		
苯、甲苯	饮料	单滴液相微萃取	GC-MS	[64]

表 2 LPME 在酒类样品中的应用
Table 2 Applications of LPME on wine samples

目标物	样品基质	萃取模式	检测仪器	参考文献
有机氯农药	白酒	溶剂棒微萃取	GC-MS-MS	[65]
赫曲霉素 A	白酒	中空纤维膜液相微萃取	HPLC	[66]
杀虫剂	白酒、啤酒	中空纤维膜液相微萃取	UPLC-MS/MS	[67]
新烟碱类杀虫剂	蜂蜜酒	分散液相微萃取-QuEChERS	LC-MS/MS	[68]
正己酸乙酯	白酒	中空纤维膜液相微萃取	GC-MS	[69]
酮类老化物质	啤酒	分散液相微萃取	HPLC	[70]
杀菌剂	酒样	分散液相微萃取	GC, GC-MS	[71]
生物胺	啤酒	分散液相微萃取	GC-MS	[72]
有机磷	酒	单滴液相微萃取	GC-MS	[73]

5.3 蔬菜、水果、粮食中不同物质的分析测定

蔬菜、水果、粮食是人们日常生活中不可或缺的食品,其农残量的控制和检测是人们关注的热点。然而它们的基质比饮料、酒类要复杂,所以对样品前处理技术的要求也更高。目前 LPME 在蔬菜、水果、粮食中的农药残留的也有不少报道。表 3 列举了 LPME 在蔬菜、水果、粮食中的应用实例。

5.4 禽畜肉及水产品中不同物质的分析测定

兽药残留问题是近年来食品检测中关注的热点问题,

发展可靠、灵敏的分析检测技术是控制兽药残留、保证食品安全的重要前提。兽药残留检测的显著特点是需要准确灵敏的样品前处理技术。目前 LPME 在兽药残留的分析中已有很多报道,另外,在农药、重金属等有害物质残留在禽畜肉及水产品中也有一些应用(表 4)。

5.5 食用油中不同物质的分析测定

LPMS 还被应用于食用油中芥酸、胆固醇及农药残留的检测中,表 5 列举了 LPMS 近几年在牛奶中的应用实例。

表 3 LPME 在蔬菜、水果、粮食中的应用
Table 3 Applications of LPME on vegetables, fruits and cereal

目标物	样品基质	萃取模式	检测仪器	参考文献
农药残留	蔬菜	中空纤维膜液相微萃取	LC-MS	[74]
酚醛酸	水果	直接单滴微萃取	GC-MS	[75]
有机磷	蔬菜	中空纤维离子液液相微萃取	HPLC	[76]
有机氯	草莓, 番茄	中空纤维膜液相微萃取	GC	[77]
	蔬菜	单滴液相微萃取	GC-MS	[78]
三唑类杀菌剂	水果、蔬菜	中空纤维膜液相微萃取	GC	[79]
除草剂	黄瓜	中空纤维膜液相微萃取	UPLC-MS/MS	[80]
农药残留	蔬菜	分散液相微萃取	GC-MS/MS	[81]
农药残留	蔬菜	单滴液相微萃取	GC	[82]
农药残留	苹果和葡萄	单滴液相微萃取	GC-MS	[83]
特丁硫磷	甘蔗	分散液相微萃取	GC	[84]
氨基甲酸酯	番茄	分散液相微萃取	HPLC	[85]
生育酚	水果、蔬菜	分散液相微萃取	HPLC, LC-MS	[86]
吡虫啉	稻米	三相中空纤维膜液相微萃取	HPLC	[87]
农药残留	玉米	分散液相微萃取	GC-MS	[88]
脱氧萎镰菌醇	面粉	分散液相微萃取	LC-DAD	[89]

表 4 LPME 在禽畜肉、水产品中的应用
Table 4 Applications of LPME on livestock and aquatic products

目标物	样品基质	萃取模式	检测仪器	参考文献
氯霉素	鱼	中空纤维膜液相微萃取	GC	[90]
有机磷	鱼	中空纤维膜液相微萃取	GC	[91]
瘦肉精	猪肉	中空纤维膜液相微萃取	HPLC	[92]
多氯联苯	鱼	分散液相微萃取	GC	[93]
氟喹诺酮	鸡肝脏	分散液相微萃取	HPLC	[94]
双酚 A	牛肉罐头, 灌装牛奶	中空纤维膜液相微萃取	HPLC	[95]
有机氯	鱼	单滴液相微萃取	GC-MS	[96]
甲基汞	鱼	单滴液相微萃取	AAS	[97]
三乙胺	鱼	单滴液相微萃取	UV	[98]
孔雀石绿和结晶紫	鱼	分散液相微萃取	HPLC	[99]

5.6 牛奶中不同物质的分析测定

牛奶中抗生素残留等问题是长期以来都存在, 且受到广泛关注的食品安全问题。建立准确、灵敏的牛奶中有害物质的检测方法, 对乳制品食品安全和奶牛疾病防控等均具有重要意义。目前 HF-LPME 在牛奶中兽药残留、抗氧化

剂、三聚氰胺等的检测中已有一些报道, 表 6 列举了 LPMS 近几年在牛奶中的应用实例。

5.7 LPME 在其他样品中的应用

LPME 在其他样品中的应用见表 7。

表 5 LPME 在食用油中的应用
Table 5 Applications of LPME on edible oils

目标物	样品基质	萃取模式	检测仪器	参考文献
芥酸	菜籽油	中空纤维两相液相微萃取	HPLC	[100]
胆固醇	牛奶、蛋黄、橄榄油	分散液相微萃取	HPLC	[101]
拟除虫菊酯类	植物油	分散液相微萃取	GC	[102]
三嗪类灭草剂	植物油	分散液相微萃取	HPLC	[103]
乙酰甲基原醇	黄油	分散液相微萃取	HPLC	[104]
酚类化合物	橄榄油	分散液相微萃取	HPLC-MS	[105]

表 6 LPME 在牛奶中的应用
Table 6 Applications of LPME on milk

目标物	样品基质	萃取模式	检测仪器	参考文献
苯氧基除草剂	牛乳	中空纤维膜液-液-液三相微萃取	GC-FPD	[106]
大环内酯类抗生素	牛奶	中空纤维液相微萃取	HPLC	[107]
雌二醇	牛奶	中空纤维液相微萃取	HPLC	[108]
三聚氰胺	牛奶	中空纤维液相微萃取	HPLC	[109]
双酚 A	奶粉	中空纤维液相微萃取	GC-MS	[110]
抗氧化剂	牛奶	中空纤维液相微萃取	HPLC	[111]
氟喹诺酮	牛奶	分散液相微萃取	HPLC	[112]
氯	牛奶	顶空液相微萃取	离子色谱	[113]
三嗪类和苯基脲类除草剂	牛奶	分散液相微萃取	HPLC	[114]

表 7 LPME 在其他样品中的应用
Table 7 Applications of LPME on other samples

目标物	样品基质	萃取模式	检测仪器	参考文献
有机氯农药	绿茶	动态中空纤维膜液相微萃取	GC-ECD	[115]
有机磷农药	绿茶、茶叶	两相中空纤维膜液相微萃取	GC-FPD	[116]
	茶叶	分散液相微萃取	GC	[117]
共轭亚油酸	芝麻	中空纤维两相液相微萃取	HPLC	[118]
苏丹红	辣椒酱辣椒、咸鸡蛋	中空纤维两相液相微萃取	HPLC LC-MS/MS	[119]
苏丹红	香肠	分散液相微萃取	HPLC	[120]
	蛋黄	分散液相微萃取	HPLC-MS	[121]
磺胺类	蜂蜜	三相中空纤维两相液相微萃取	LC-MS/MS	[122]
		分散液相微萃取	HPLC	[123]
生物胺	虾酱、番茄酱	三相中空纤维两相液相微萃取	HPLC	[124]
氯霉素、甲砒霉素	蜂蜜	分散液相微萃取	HPLC	[125]
苯甲酸、山梨酸	酱油	顶空液相微萃取	CE	[126]
			HPLC	[127]

6 结 论

综上所述,液相微萃取是一种新型环境友好型样品预处理技术,它集萃取、富集、净化于一体,具有选择性好、操作简单、快速、富集倍数高、所需有机溶剂用量少等特点。今后随着更多萃取方式、萃取溶剂的开发,将会有更多样的萃取模式进行高效和快速分析,与各仪器联用的自动化程度也将进一步加强,液相微萃取技术在较为复杂的食品检测、药物分析、生物样品分析方面将发挥越来越大的作用,在环境、医药、植物成分分析以及各种组学研究等领域里也将有着广阔的应用前景。

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