简述分散液相微萃取技术

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摘 要: 现代化学分析要求分析过程简单、小型化、自动化, 尤其是快速处理样品。分散液相微萃取有助于满足这些要求, 它是最近发展起来的一种新型样品前处理技术, 具有操作简单、快速、成本低、试剂消耗少, 回收率和富集效率高等特点。分散液相微萃取可与高效液相、气相、原子吸收联用, 而且在食品安全分析中得到广泛应用。本文对分散液相微萃取的基本原理、萃取过程、影响因素(如萃取剂和分散剂的类型和体积、萃取时间和电解质)和目前在食品安全中的应用进行了评述。

关键词: 分散液相微萃取; 化学分析; 食品安全; 方法研究

A review on the dispersive liquid-liquid microextraction

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ABSTRACT: One of the most important objectives of modern analytic chemistry is miniaturization, simplification and automation of the whole analytic procedure, especially to speed up sample treatment. Dispersive liquid-liquid microextraction (DLLME) has greatly contributed to meet this objective, which is a technical method developed recently for sample-preparation , and is simple for operation, fast, and inexpensive, with a high enrichment factor and low consume of volume of organic solvent**.** DLLME coupled with high performance liquid chromatography (HPLC), gas chromatography (GC) and atomic absorption spectrometry (AAS) have been widely applied to the analysis for food safety. The basic principles, influence factors (e.g., types and volumes of extraction and disperser solvents, extraction time, and electrolyte) and the latest applications of DLLME in food safety area are reviewed.

KEY WORDS: dispersive liquid-liquid microextraction; chemical analysis; food safety; method research

1 引 言

传统的样品前处理方法有多种, 如蒸馏、层析、索式提取、液萃取, 近些年又有一些新的技术发展起来, 液液微萃取[1](liquid–liquid microextraction, LLME)、单滴微萃取[2-3](single drop microextraction, SDME)、浊点萃取[4](cloud point extraction, CPE)、固相微萃取[5] (solid-phase microextraction, SPME)、搅拌棒吸附粹取[6](Stir bar for sorptive extraction, SBSE)、微波辅助萃取[7](microwave-assisted extraction, MAE)、双相透析[8](bipolar dialysis, BD)、超临界流体萃取[9](supercritical fluid extraction, SFE)。这些方法, 普遍存在重复操作、劳动强度大、用时较长, 使用大量对

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人体和环境有毒、有害的有机溶剂, 萃取易发生乳化现象、难以实现自动化以及消耗大量试剂等缺点[10]。因此样品的前处理需要改进, 改进的方向主要有: 实验过程的微型化、操作的自动化、减少试样和试剂的使用、提高萃取效率和增大富集倍数等。2006 年, Rezaee[11]等首次报道了一种新型样品前处理技术, 即分散液相微萃取(dispersive liquid–liquid microextraction, DLLME), 它与均相液液萃取(homogeneous liquid–liquid extraction, HLLE)和 CPE 相似, 是建立在三相溶剂体系基础之上的萃取技术。DLLME 最大的优点就是传质速度快, 并且该方法集采样、萃取和浓缩于一体, 避免了固相微萃取中可能存在的交叉污染的问题, 是一种操作简单、快速、成本低、试剂消耗少、回收率和富集效率高等优点。作为一种食品安全分析的样品前处理新技术, 其在痕量分析领域具有广泛的应用前景。

2　分散液相微萃取技术的原理

分散液相微萃取相当于微型化的液液萃取, 是基于目标分析物在样品溶液和萃取剂之间平衡分配的过程。萃取剂在分散剂的作用下形成分散的、极细的有机小液滴。经过一段时间之后, 被分析物在有机相和水相两相之间达到分配平衡。当系统达到平衡之后, 萃取在有机液滴中的被分析物的量可由下式计算。

$$n= K_{odw}V_d\ C_oV_s/(K_{odw}V_d+V_s);$$

其中 n 为有机溶剂萃取到的分析物的量;

C_o 为分析物的初始浓度;

K_{odw} 为分析物在有机液体与样品之间的分配系数;

V_d,V_s 分别为有机液体、样品的体积。

由公式可见, 有机液滴体积越大, 萃取被分析物的量就越大。但由于分析物进入液滴的过程是扩散过程, 液滴体积越大, 则萃取速率越小, 达到平衡所需的时间也就越长。由于形成了混浊液, 萃取剂与样品溶液之间的接触面很大, 因此会快速达到平衡, 所需的萃取时间很短[11,12]。

分配系数 K 是指达到平衡时, 目标分析物在萃取剂和样品溶液中浓度的比值。分散液相微萃取只适用于亲脂性高或中等的分析物(K>500), 对于高度亲水的中性分析物, 是不适用的; 而对于具有酸碱性的分析物, 可通过控制样品溶液的 pH 值使分析物以非离子化状态存在, 从而提高分配系数[13]。

3　分散液相微萃取的萃取过程

分散液相微萃取的萃取过程如图 1 所示: 在带塞的离心试管中加入一定体积的样品溶液(水相)(A), 将含有萃取剂的分散剂通过注射器或移液枪快速地注入离心试管中, 轻轻振荡, 形成一个水/分散剂/萃取剂的乳浊液体系(B)后, 萃取剂被均匀地分散在水相中, 与待测物有较大的接触面积, 待测物可以迅速由水相转移到有机相并且达到两相平衡。最后通过离心使分散在水相中的萃取剂沉积到试管底部(C), 用微量进样器吸取一定量的沉积相后直接进行分析检测(D)。

Chen[14,15]等提出通过加入分散剂作为去乳化剂打破 O/W 型乳化液, 达到相分离的作用, 然后收集上清液, 此法不需要离心, 如图 2 所示。Guo[16]等也应用 DLLME-GC–MS 联用测定 16 种多环芳烃, 优点可以省去一些步骤离心, 不需要特殊的萃取装置。但 Zacharis[17]等也提出存在消耗大量的分散试剂, 使分析物部分不溶于水相的缺点。

4　影响分散液微萃取技术的因素

影响分散液微萃取技术萃取效率的因素有很多, 可以使用单变量方法对影响因素逐个地进行最优化选择分散液微萃取技术的影响因素主要包括萃取剂的种类和剂量、分散剂的种类和剂量、螯合剂的浓度、萃取时间、电解质等。

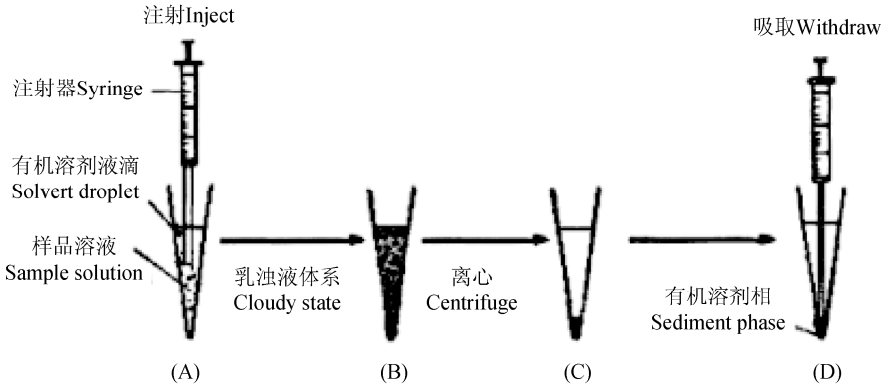
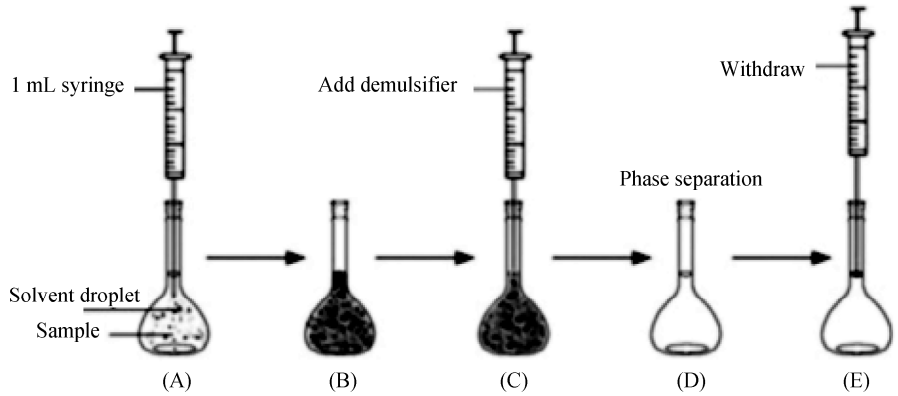


图 1　分散液相微萃取的操作步骤

Fig. 1　Procedure of dispersive liquid-liquid microextraction



(注: A 萃取剂和分散剂注射到样品中; B 形成乳浊液; C 加入终止剂打破乳浊液; D 相分离; E 在上清)

图 2 分散液相微萃取的操作步骤

Fig. 2 Procedure of dispersive liquid-liquid microextraction

4.1 萃取剂的种类和体积

分配系数和选择性是控制萃取剂选择的重要参数, 选择性是指溶剂对目标组分的获得能力, 萃取剂必须对目标分析物的萃取能力强。萃取剂应满足一下几点: 1)在最佳液相色谱条件下有较好的色谱行为或易蒸发可以除去, 并在注入色谱系统的过程中不产生对目标物干扰的峰; 2)有比水的密度; 3)萃取能力; 4)在水中的低溶性, 而且在分散剂存在的条件下能够形成两相。

目前, 据文献报道, 当萃取剂的密度比水低时, 依此采取以下几种方法: 1)浮动的有机液滴的凝固[18]; 2)在特殊装置里分离和有机相的收集; 如图 3(A)[19](B)[20]; 3)纳米粒子的吸附[21]。4)助溶剂, 当萃取剂的密度小于水的密度时, 使用助溶剂使混合物的密度大于水的密度[22]。

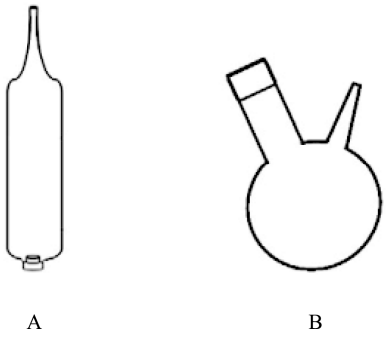


图 3 萃取特殊装置

Fig. 3 Special device for extraction

分散液微萃取技术的沉淀相的体积是与萃取剂的量有关的, 当萃取剂的量增加时, 沉淀相的体积也随之增加。同时, 在萃取平衡时, 沉淀相中的目标物浓度会随之减小, 富集倍数也减小了。因而要获取较高的富集倍数, 萃取剂的量要较小。所以在分散液微萃取中, 萃取剂的剂量是很少的(μL 级), 少至 15 μL[23]。

萃取剂的体积对 EF 的影响也很大, 随着萃取体积的增大, 通过离心所获得的有机相的体积是增加的, 导致在有机相中的目标分析物的浓度减小, EF 减小, 最佳的萃取剂的体积应该能确保高的 EF 和离心后有足够的沉淀相用于接下来的分析。

常用的萃取剂有四氯化碳、氯仿、二氯甲烷、四氯乙烯、氯苯、1,2-二氯苯、溴乙烷、溴苯及二硫化碳。Yousefi 等[24]应用 1-己基-3-甲基咪唑六氟磷酸盐[Hmim][PF_6], 作为萃取剂去收集和测定无机物质。另外, Anthemidis[25]应用脂肪醇(如十一烷醇)作为萃取溶剂取代了有毒的有机溶剂, 减少对环境的副作用。

4.2 分散剂的种类和剂量

DLLME 中, 分散剂起着桥梁作用: 分散剂内溶解的萃取剂随着分散剂体积的扩张而释放出来, 当扩张的分散剂溶于样品溶液时, 萃取剂部分析出形成细小的有机液滴, 分散剂减小萃取剂液滴体积, 平衡增大萃取剂的表面积, 快速达到萃取平衡在较短时间内完全萃取。由于萃取剂有较高的表面张力, 需剧烈的震动才形成小液滴[26]。同时, 分散剂的剂量直接影响浑浊液的形成和萃取剂在水相中的分散度, 进而影响到目标物的富集倍数。随着分散剂的量增加, 萃取剂在水中的溶解度也增大, 沉淀相的体积也随之减小。同时, 分散剂的剂量也会影响目标物的水溶性, Liang 等[27]提出当分散剂的剂量较少时, 不能够对萃取剂起到分散的作用, 也不能完全形成浑浊液。反之, 分散剂的剂量过大时, 目标物在水中的溶解度随着分散剂的剂量的增大而增大, 萃取率较低。因而, 为了获得恒定体积的沉淀相, 分散

剂的剂量需随着萃取剂的量的改变而改变, 并且选择合适的分散剂的剂量对分散液微萃取过程是很重要的。

此外分散剂还需满足 3 个条件: 一是分散剂必须与萃取剂、水样都有很好的相溶性, 这种混溶性是萃取剂在水相中形成乳浊液的关键; 二是萃取剂在分散剂中的分配系数要大于其在样品溶液中的分配系数; 三是有较好的色谱行为。常用的分散剂主要有丙酮、甲醇、乙腈、四氢呋喃和乙醇。

4.3　萃取时间

萃取时间对于很多萃取反应来说都是一个很重要的影响因素, 会直接影响萃取率。分散液微萃取的萃取时间是指从开始形成浑浊液到进行离心分离的这段时间[28]。萃取剂以细小的液滴的形式均匀地分散到溶液中, 由于此时有机相与水相的接触面积很大, 在很短的萃取时间内, 目标物就能达到萃取平衡。所以, 对于分散液微萃取而言, 萃取时间对萃取效率的影响不大。在分散液微萃取过程中, 离心分离耗费的时间也较短, 通常为 15~20 min。此外在萃取过程中可引入外场加快传质速率, 如超声、微波、电场等。

4.4　电解质

在液液萃取过程中, 加入电解质可产生两种共存现象[29]。

(1)盐析效应, 由于电解质在水溶液中的水合作用, 使自由水分子的浓度降低, 从而有利于溶质分析物的萃取。

(2)随着溶液的离子强度增加, 增强了极性溶质同离子之间的静电作用力, 进一步导致传质能力降低。从而使目标物和萃取剂在水相中的溶解度降低[30]。另一方面, 随着盐浓度的增加, 有机相的体积减小, 因而目标物的浓度和富集因数减小。但电解质的加入没有影响萃取的效率。

5　分散液相微萃取的应用

新的样品制备方法, DLLME 能够与气相色谱仪(GC)、高效液相色谱仪(HPLC)、原子吸收分光光度计(AAS)联用。它广泛应用分析有机和无机化合物, 本文着重于介绍在食品安全中的应用, 如下表。

表 **1**　分散液相微萃取的应用

Table 1　Applications of dispersive liquid-liquid microextraction

分析物	样品	检测器	萃取剂及计量 μL	分散剂及计量 mL	富集倍数	检出限 $\mu g\cdot kg^{-1}/\mu g\cdot L^{-1}$	回收率%	RSD%	文献
百菌清、克菌丹、	葡萄	GC	氯苯 10.0	丙酮 1.0	788~876	6.0~8.0	92.3~106.1	-	[31]
特丁硫磷残留	甘蔗	GC	三氯乙烷 22	丙酮 1.0	456.03	20	84.4~90.31	3.19~5.88	[32]
硫化合物	葡萄酒	GC-MS	二氯甲烷 150	-	3.57~61.15	0.36~1.67	91.99~125.87	3.27~12.38	[33]
多氯联苯	鱼	GC	氯苯 30	丙酮 1	87~123	0.12~0.35	81.2~108.	2.2~8.6	[34]
6-邻苯二甲酸酯	牛奶	GC	CCl_4 40	甲醇 0.8	220~270	0.64~0.79	93.2~105.7	＜4	[35]
农药残留	番茄	GC-MS	CCl_4 100	乙腈 10	-	1.4~9.6	70~110	1~20	[36]
羟基二苯乙烯	葡萄酒	GC-MS	醋酸酐 20	丙酮 0.5	-	-	90~102	＜12	[37]
农药残留	蜂蜜	GC-MS	氯仿 50	乙腈 0.75	36~114	0.4~3	75~119	5~20	[38]
农药残留	苹果汁	GC-MS	CCl_4 100	乙腈 0.75	36~114	0.06~2.2	60~105	1~21	[39]
盐酸克伦特伦	猪肉组织	HPLC	$C_2H_2Cl_4$ 150	甲醇-氨 0.5	62	0.07	87.9~103.6	＜3.9	[40]
胆固醇	蛋黄等	HPLC	$CCl_4$35	乙醇 0.8	-	0.01	>95.0	≤3.1	[41]
氯霉素、甲砜霉素	蜂蜜	HPLC	1,1,2,2-四氯乙烷 30	乙腈 1	68.2~87.9	0.1~0.6	91.7~98.1	4.3~6.2	[42]
生物胺	黄酒	HPLC	1-辛醇 50	—	—	0.02~5	95.42~104.5	2.4~3.2	[43]
BHA、BHT	果汁	HPLC	2-乙基-1-己醇 200	丙酮 0.55	208、203	2.5、0.9	95~99.6	＜4.7	[44]
八种农药	香蕉	HPLC	$[C_6MIM][PF_6]$88	甲醇 0.714	—	0.320~4.66	69~97	＜8.7	[45]
铅、镉	自然水	ETAAS	二甲苯/甲醇 0.2%	甲醇 0.9	80、42	0.01、0.002	93.7~97.9	3.8~4.2	[46]
钴、镍	大米	GFAAS	CCl_4 15	丙酮 1	101~200	0.033	97、109	7.5、8.2	[47]

GC: Gas Chromatography
HPLC: High-performance Liquid Phase Chromatography
GFAAS: Graphite Furnace Atomic Absorption Spectrometry
ETAAS: Electrothermal Atomic Absorption Spectrometry

6 展 望

DLLME 技术是一种新型的样品前处理技术，与传统的萃取方法相比具有操作简单、快速、准确、成本低、对环境友好且回收率高和富集倍数高等特点。此技术在未来将会随着萃取剂范围的扩大而使用更多的底物，而且更多与之联用的技术，为食品微量分析提供更广阔的前景。

食品分析面临分析物浓度低、基质干扰物多且组成复杂等问题，而传统的样品前处理方法由于操作繁琐耗时，有机溶剂用量大，灵敏度低等已不能满足现代分析化学发展的需要，因此，发展快速、高效、环境友好的新型样品制备技术显得非常有意义。分散液微萃取技术因操作简单、灵活省时、高效精确、环境友好等特点，并通过操作模式不断的发展及与多种新型样品前处理方法的联用，在食品分析领域中展现出愈来愈广阔的应用前景。

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“食药用菌”专题征稿函

我国发现和利用食用菌已有数千年的历史，其中大型真菌作为药物使用也至少有 2500 年的历史。食用菌营养丰富，优质蛋白质含量较高，含有人体所需的 8 种必需氨基酸，其中赖氨酸和亮氨酸的含量尤为丰富。另外，食用菌还含有多种活性多糖、微量元素等功能性物质，具有特殊的保健功能。药用菌也具有良好的药理活性，具有调节免疫力，增强记忆力，延缓衰老，减少心脑血管疾病发生等功效，应用十分广泛。随着人们对食药用菌营养价值的认可，对食药用菌产品的消费需求也不断增加，因此食药用菌食品具有很高的开发价值。

我国食药用菌年产量占世界总产量的 75%以上，其总产值在我国种植业中排名第六位，主要栽培种类有 70~80 种，形成商品的有 50 种，具有一定生产规模的有 20 种以上。总产量年均复合增长率约为 12.40%，总产值年复合增长率约为 17.01%。鉴于此，本刊特别策划了“**食药用菌**”专题，由中国工程院院士、中国吉林农业大学食药用菌专家**李玉教授**担任专题主编，**李教授**为原中国菌物学会理事长，中国食用菌协会副会长，国际药用菌学会理事长，食药用菌教育部工程研究中心首席科学家，国家食用菌产业技术体系岗位科学家兼资源收集与繁殖利用功能实验室主任。围绕“**食药用菌的化学组成、理化性质、保鲜贮藏、食药用菌中有害物质检测、食药用菌的深加工、食药用菌营养特性的研究、食药用菌功能特性的研究、食药用菌标准与体系等**或您认为本领域有意义的问题展开讨论，计划在 2016 年 2 月出版。

鉴于您在该领域的成就，本刊编辑部及**李玉教授**特邀请您为本专题撰写稿件，以期进一步提升该专题的学术质量和影响力。综述、实验报告、研究论文均可，请在 2016 年 1 月 30 日前通过网站或 E-mail 投稿。我们将快速处理并优先发表。

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