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REVIEW

Progress of Extraction Solvent Dispersion Strategies for Dispersive Liquid-liquid Microextraction

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Abstract: Dispersive liquid-liquid microextraction (DLLME) is a new sample preparation technique emerging recently. The dispersion of organic extraction solvent at micro-liter level in aqueous samples is the key step in DLLME. The published strategies of dispersion for DLLME are roughly classified into three types in terms of the instruments used and dispersion principles, namely physical dispersion method, in-situ chemical reaction-based dispersion method and new dispersion medium-based dispersion method. The physical dispersion method includes mechanical shaking method, ultrasound/microwave-assisted method and solubility-adjustment method. The in-situ chemical reaction method is referred to the two modes, in which either the dispersed extraction solvent is formed by in-situ chemical reaction or the dispersion of extraction solvent is achieved by the gas generated from chemical reactions. The new dispersion medium-based dispersion method uses some non-volatile substances, such as medium-chain saturated fatty acids, ionic liquid, surfactant and kapok fiber fragments, to substitute the dispersive solvent used in conventional DLLME. A total of 96 relevant literatures are cited in this review and the prospects of DLLME are highlighted.

Key Words: Dispersive liquid-liquid microextraction; Physical dispersion; In-situ chemical reaction; Non-volatile solvent; Review

1 Introduction

Since the invention of dispersive liquid-liquid microextraction (DLLME) as a novel sample preparation technique in 2006[1], it has obtained considerable attention from analytical chemical researchers, due to its distinct merits of excellent green chemical indices and enrichment factors in the magnitude of several hundreds. More than 1000 scientific articles related to the DLLME technique were published[2], including some reviews on the topic of DLLME[2–11]. The breakthrough progresses of DLLME in recent years were outlined in these reviews. However, as far as we know, there was no specific discussion on the strategies of dispersion of extraction solvent yet.

The crucial step in DLLME is to completely disperse the extraction solvent at micro-liter level in the aqueous sample solution. In this review, various methods for dispersion of extraction solvents are summarized. The strategies of dispersion in DLLME are roughly classified into three types in terms of the instruments used and dispersion principles, namely physical dispersion method, in-situ chemical reaction-based dispersion method and new dispersion medium-based dispersion method. To avoid the loss of extraction solvent and the decrease of extraction efficiency induced by excessive dispersion solvent, DLLME based on a ternary solvent system (aqueous sample solution, extraction solvent and dispersion solvent) in early stage is replaced by DLLME based on a binary solvent system (sample solution and extraction solvent). To simplify operation procedure and reduce dependence on devices in DLLME, in-situ chemical reaction-based dispersion method and new dispersion medium-based method are introduced instead of previous DLLME assisted by some devices such as micro-wave oven and ultrasonic cleaner. To further strengthen the characters of

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green chemistry in DLLME, on-line combination of DLLME with consequent instrument analysis is nowadays preferable to the previous off-line DLLME.

2 Dispersion methods

2.1 Physical dispersion methods

2.1.1 Mechanical shaking dispersion methods

Mechanical shaking dispersion methods use external force to shake extraction mixture violently, and an emulsified solution is obtained. Mechanical shaking dispersion methods can be classified into five main groups: manual[12], vortex[13], up-and-down-shaker[14], magnetic stirring[15] and air-assisted[16] shaking methods. Typical examples of mechanical shaking dispersion are presented in Table 1.

Manual shaking method is the simplest method. Because the effective dispersion of extraction solvent would not be achieved merely by manual shaking, it is always used in combination with other dispersion methods. Huang *et al*[17] found that manual shaking followed by sonication could enhance the extraction efficiency and shorten the sonication time. Tsai *et al*[18] reported that fine dispersive emulsification solution was obtained by 90 s-violent shaking of the mixed aqueous sample composed of extraction solvent, dispersive solvent and sample. The experiment results from many reports[19–23] indicated that addition of water-soluble inorganic salt aided in sufficient dispersion of extraction solvent at microliter level into aqueous phase. Ma *et al*[20] found that 1 min-manual shaking was able to form emulsion when Na_2SO_4 was added to the mixed solution of aqueous sample and extraction solvent of dichloromethane.

Obviously, the poor stability of manual shaking often results in discrepancy of analysis results between samples. In vortex-assisted method, the dispersion of the extraction solvent is achieved by vortex mixing instead of manual shaking, and the uniformity is improved obviously. Seebunrueng *et al*[24] used vortex method to enhance the dispersion efficiency of low-density extraction solvent. In 2015, this group[25,26] modified the method (Fig.1a) with no use of the dispersion solvent to avoid the possible decrease in extraction efficiency caused by dispersion solvent and furthermore, by using $AlCl_3$ as demulsifier, the consumption of organic solvent was reduced and centrifugation was not needed. In Gure *et al*'s report[13], it took only 30 s to obtain a well dispersed emulsion by the aid of vortex. As vortex-assisted method can treat only one sample in a single run, it is not suitable for processing large numbers of samples.

The sample solution and extraction solvent could be effectively mixed by the vigorous motion on up-and-down-shaker. This dispersion method processed batches of

Table 1 Physical dispersion for DLLME

Extraction method	Apparatus	Analytes	Extraction (dispersion) solvent	Extraction time (min)	Phase separation technique	Enrichment factor	Ref.
Mechanical shaking dispersion method							
MS-USAEME	UHPLC-PDA	Nitrophenols	1-undecanol (—)	3.0	Centrifugation	62–500	[17]
DLLME-LSC	GC-MS	Organochlorine pesticides	Tetrachloroethylene (TBME)	1.5	Centrifugation	1885–2648	[18]
SA-DLLME	PTV-GC-MS	Haloacetonitriles	Dichloromethane (—)	1.0	Centrifugation	22–114	[20]
VA-DLME–SID	HPLC-PAD	Organophosphorus pesticides	1-dodecanol/hexane (—)	1.0	$AlCl_3$ as a demulsifier	180–282	[25]
VA-IL-DLLME	Capillary HPLC-DAD	Sulfonylurea herbicides	$[C_6MIM][PF_6]$ (methanol)	0.5	Centrifugation	—	[13]
UDSA-DLLME	GC-MS	Polycyclic aromatic hydrocarbons	1-heptanol (—)	3.0	Centrifugation	392–766	[31]
UDSA-DLLME	GC-MS	Triazine herbicides	1-hexanol (—)	1.0	Centrifugation	361–1391	[27]
DSME	GC–MS	Polycyclic aromatic hydrocarbons	Toluene (—)	104 s	Magnetic stirring induces vortex	35–55	[28]
MS-IL-DLLME	GFAAS	Vanadium	$[C_4MIM][PF_6]$ (—)	—	Centrifugation	125	[63]
In-syringe MSA-DLLME	Photomultiplier tube	Aluminum	n-hexanol (—)	40 s	Droplet flotation	33	[15]
AA-DLLME	GC-FID	Phthalate esters	1,1,2,2-tetrachloroethane (—)	< 1	Centrifugation	889–1022	[16]
Flow-batch SI-DLLME	UV/Vis spectrophotometer	Thiocyanate ions	Amyl acetate (acetonitrile)	3 s	Self-sediment	—	[64]
Automated DLLME	GC-MS	Phthalate esters	Toluene (acetonitrile)	2.0	Dispersant as demulsifier	178–272	[32]
SV-SIA-DLLME	Stopped-flow spectrophotometry	Boron	n-amylacetate (—)	—	Self-separation	—	[33]