Journal of Food and Drug Analysis

Volume 8 | Issue 4 Article 2

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Journal of Food and Drug Analysis, Vol. 8, No. 4, 2000, Pages 235-247 藥物食品分析 第八卷 第四期

An Overview of Supercritical Fluid Extraction in Chinese Herbal Medicine: from Preparation to Analysis

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(Received: July 20, 2000; Accepted: November 15, 2000)

ABSTRACT

A review concerning the use of supercritical fluid extraction (SFE) in the preparation and analysis of Chinese herbal medicine (CHM) is presented. The literature review foresees the trend of increasing use of SFE in CHM preparation. The application examples in the preparation of useful ingredients and analysis of pesticide residues are discussed. The use of SFE CO_2 to replace traditional organic solvent is justified and promising. Consideration is given to the coupling of sub-critical H_2O and supercritical CO_2 to extract more compounds and to use the dual role of extracting useful ingredients and removing pesticide residues. Careful integration of laboratory SFE results into the design and implementation of factory production is beneficial in ensuring the successful use of SFE in CHM.

Key words: Chinese herbal medicine, supercritical fluid extraction, useful ingredients, effective ingredients, pesticide residues

INTRODUCTION

The increasing use of Chinese herbal medicine (CHM) worldwide, the controversial health effects of CHM, and the conventional means of preparing CHM have raised public concern on their safety, efficacy and quality. The safety of CHM to consumers has become a major requirement of any new CHM. Many CHM are used in concentrated form prepared by extracting the active ingredients from their original plant matrices. The origin of the raw plants and the soundness of extraction procedures often dictate the efficacy of the concentrated form. The quality is assured by implementing a quality control and assurance system at all stages from the manufacture to the point of sale. The CHM industry responds to these challenges in part by improving conventional extraction procedures and implementing testing procedures prior to product introduction into the market place[1].

Steam distillation or solvent extraction, usually with an organic solvent, is the procedure conventionally used to prepare the concentrated extracts. The removal of the solvent from the extract is needed in the latter case. Minimization of the amount of residual solvent is a critical process. The residual level must be kept below the regulatory level without the expense of heavily loss or degradation of the effective ingredients. Current regulations stating the extracting solvents in the production of foodstuffs and food ingredients are generally regarded as safe, i.e., any residues or derivatives present in the product in technically unavoidable quantities presenting no danger to human health, in compliance with good manufacturing processes. For example, the acceptable extraction solvents under European Community (EC) directive 84/344/EEC include acetone, butane, butyl acetate, carbon dioxide, ethanol, ethyl acetate, nitrous oxide and propane[2]. The extraction solvents for use as carriers and processing, aides foodstuffs in the USA under 21 CFR FDA include acetone, dichloroethene, dichloromethane, ethyl acetate, hexane, methanol, 2-proponol and trichloroethene[2]. The choice of extraction solvent in the preparation of ingredients for foodstuffs is generally limited by the safety regulations. Similar limitations are anticipated for CHM.

Supercritical fluids (SF) possess gas-like properties of diffusion, viscosity, and surface tension, and liquid-like density and solvating power. These properties, which could be altered through suitable temperature and pressure changes, combine to form a unique medium that is advantageous to perform extraction process. The term “destraction” when discussing SF was used to highlight the similarity of the technique to both volatility-based distillation and solubility-based extraction. Several advantages are obtained when using carbon dioxide in supercritical fluid extraction (SFE): selectivity, speed and efficiency, oxygen-free environment, minimal post-extraction manipulation, low operating temperature, and low toxicity[3]. Despite these promising features, the applications of SFE in CHM are limited[4, 5]. The matrices encountered in the extraction and analysis of CHM were usually dried plants (single-component) or a mixture of dried plants (composite-prescription). Mostly are in powder form. However, matrices similar to CHM, such as food and natural product matrices, were frequently extracted and analyzed using SF CO_2[6~11].

The efficiency of SFE is determined by parameters such as modifier type and amount, extraction pressure, extraction temperature, extraction time etc. Higher extraction pressure usually provides higher fluid density, which in turn increases the solvating power. The upper pressure limit is dictated by the safety regarding high pressure. Increasing extraction temperature usually decreases the interaction between matrix and analytes, which results in better extraction efficiency. The prevention of degradation of thermally labile analytes dictates the upper temperature limit. Static extraction means

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soaking the sample in the supercritical fluid to achieve the equilibrium state between fluid, matrix and analytes. Static extraction is preferred in situations dealing with low concentrations of analytes strongly bound to the matrix. For dynamic extraction, fresh supercritical fluid is continuously passing through the sample. The target compounds remain unsaturated in the fluid. The mass transfer efficiency of target compounds from sample matrix to fluid is enhanced. The optimal static and dynamic extraction time is usually determined by compromising the extraction efficiency and the consumption of supercritical fluid. The most popular used fluid, carbon dioxide, is fully non-polar. To extend the classes of extractable analytes, various organic solvents are spiked into the extraction cell or simultaneously delivered with CO_2 fluid as a co-solvent and which functions as a modifier to increase the polarity of the supercritical fluid. The modifier type and amounts are the most critical parameters determining extraction efficiency. To collect volatile compounds, a low-temperature trapping device is needed. The fore-mentioned experimental parameters might synergistically affect the extraction efficiency. An experimental design is usually preferred before initiating an optimization experiment.

Below is a review of the current state of SFE in CHM and similar matrices considering applications in preparation and analysis, the possible solutions to the drawbacks, and foreseeable trends. Successful applications of SFE require the proper use of many experimental parameters. Specific experimental parameters used to fulfill the designed purposes were organized to facilitate the development of SFE-based process and method in future work.

Literature Search

We have carried out a literature review by searching the Science Citation Index (SCI) from the Institute for Scientific Information (ISI). We searched for literature published between 1990 and May 2000 and which contained the terms “fluid extraction” or “SFE” in the fields of keywords and titles. The database used was the ISI CD-ROM edition for the years between 1990 and 1995, whereas the web of science edition was used thereafter. For literature published in 1993, we also searched abstracts. Only literature dealing with herb preparation and pesticide analysis was considered relevant and counted. The search results were plotted as the number of publications in herb or pesticide vs. the publishing year, shown in Figure 1. The number of works using SFE in herb preparation appears to be constant and limited before 1996. A consistent increase of literature is observed after 1996, indicating that SFE is becoming popular. This might be due to the increasing availability of commercially available SFE instruments. Literature using SFE for pesticide analysis is significantly less than for herb preparation. The number of relevant works appears to decrease after 1999. This might be attributed to the limited number of targeted pesticides compared to the vast number of herbs and their effective and extractable ingredients. Based on this observation, we infer the foreseeable trend of SFE applications in CHM will focus on preparation rather than on analysis.

Sfe of Useful Ingredints from Herbs and Plants

Table 1[12~32] and 2[33~53] lists the application examples of SFE of useful ingredients from herbs and plants, respectively. The corresponding SFE parameters, analytical method, recovery (or yield) and reference are also listed. Detailed inspection of these applications reveals that most applications extract the useful ingredients at pressure greater than 200 atm and temperature between 40 and 80˚C. Methanol and ethanol ranging from 3 ~ 20 % are the mostly used modifier. Static extraction was frequently used to overcome the strong affinity of useful ingredients to the matrices. The extraction time was usually 15 min for static extraction and less than 40 min for dynamic extraction. The chemical structures of the useful ingredients derived from different plants are quite different. From the viewpoint of using SFE, the polarity of these ingredients is a good indicator for selecting an appropriate SFE experimental condition. The polar ingredients usually possess functional groups such as hydroxyl, carboxylic or amine. The more polar the ingredients, the larger the amounts of modifiers needed. The same guidance is also applied to the SFE of pesticide residues. It has been observed that sub-critical H_2O is becoming an alternative SF for CO_2[49, 53]. The increasing use of SF H_2O in the extraction of useful ingredients from herb and plant matrices is foreseen. The use of a two-stage extraction scheme also promises to increase the purity by filtering out the impurities at the first stage[46]. The integration of preliminary results from laboratory SFE to a pilot or even factory preparation is not very common. More research is needed in this aspect to ensure successful factory production.

One of the drawbacks with SFE is that it fails to achieve the same extracting efficiency when extracting real samples as extracting synthetic samples. This might be because the synthetic samples used for process development do not represent the real sample well. This criticism usually lacks sufficient data needed to downgrade the usefulness of SFE. A comparison of the extraction efficiency of useful ingredients from real samples between SFE and conventional extraction means might provide more scientific evidence. The results

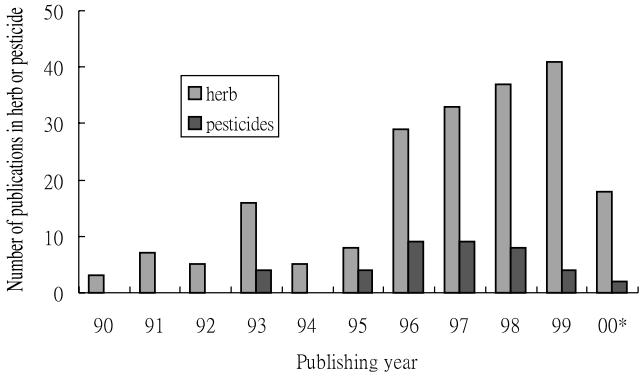

Figure 1. The searching results plotted as number of publications in herb or pesticide vs. publishing year. (*till May)

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Table 1. SFE of useful ingredients from herbs

Useful ingredients	Herb	SFE parameters	Analytical method	Analytical figure of merits	Reference
	frankincense, myrrh, *Evodia rutaecarpa*	pressure: 198 atm temperature: 50˚C time: dynamic < 45 min. flow rate: 4 kg/hr	GC-MS		4
artemisinin, artemisinic acid	aerial parts of *Artemisia annua*	pressure: 150 atm temperature: 50˚C time: < 20 min. modifier: 3% EtOH trap: EtOH	SFC-ELSD	content 0.88-1.49% (dry weight) 0.13-0.19% (dry weight)	12
artemisinin, artemisinic acid	*Artemisia annua* L.	pressure: 149 atm temperature: 50˚C time: 20 min. modifier: 3%EtOH, MeOH flow rate: 2 mL/min trap: MeOH	SFC-FID	content 0.13-0.96% 0.07-1.43%	13
antioxidants	aromatic herbs	pressure: 300 atm temperature: 40˚C time: static 5 min. dynamic 25 min. 0.4-0.5 mL/min trap: -20˚C	β-carotene bleaching test		14
ginkgolide A, B, C, J bilobalide	ginkolide standard extracts	pressure: 335 atm temperature: extractor 45˚C; restrictor: 100˚C; trap: 80˚C; time: static 5 min. dynamic 40 min. modifier: 10% MeOH trap: 400mg silica gel	GC/FID	recovery 98.6-102.3%	15
	Clivia miniata(Lindl.) Regel, *Ekebergia capensis* Sparrm., *Grewia occidentalis* L. *Asclepias fruticosa* L.	pressure: 200-400 atm temperature: 80˚C time: static 50 min. dynamic 20 min. modifier: 400 μL water flow rate: 18 mL/min at 150 atm	on-line bioassay to determine uterotonic effect	extracts obtained at 400 atm having best activity	16
ginkgolide A, B, C, J, bilobalide (SFC)	ginkgolide extracts	pressure: 280 atm temperature: 40˚C flow rate: 3.5-4 mL/min modifier: 12% MeOH in CO_2	SFC-ELSD		17
vitamin E	*Hordeum vulgare* L.	pressure: 23.69 Mpa temperature: 40˚C time: dynamic 60 min. flow rate: 0.88 g/s density: 0.921 g/mL modifier: none	HPLC	yield 1.56-4.38% (lipid-base)	18
	Australian-grown ginger	density: 0.8 g/mL time: static 3 min. dynamic 30 min. flow rate: 1 mL/min trap: $CHCl_3$	GC-FID, GC-MS		19
pungent compounds	ginger	temperature: 40˚C time: static 3 min. dynamic 30 min. density: 0.85 g/mL flow rate: 1 mL/min trap: 1g $CHCl_3$	LC-MS, ESI-MS, GC-MS	70 g/kg for 6-ingerol <2 g/kg for 6-shogaol	20
nonacosan-10-ol α-amyrin acetate squalene and stigmasterol	aerial parts of *Ephedra sinica* Root bark of *Morus alba* entire plant of *Spirodela polyrhiza*	When pressure > 198 atm, yield increased with increasing temperature; when temperature = 40 or 50˚C, best yield	GC	yield 18.42-0 mg/5g	21

Table 1. Continued

Useful ingredients	Herb	SFE parameters	Analytical method	Analytical figure of merits	Reference
		obtained when pressure < 149 atm, flow rate: 200-300 mL/min $SFCO_2$ extraction: 40˚C, 297 atm time: 10 hr; CO_2 800 L (25˚C, 1.00 atm)			
podophyllotoxin	*Dysosma pleiantha* roots	pressure: 337 atm temperature: 80˚C time: static10 min. dynamic 20 min. flow rate: 1 mL/min modifier: 4% MeOH trap: MeOH (20˚C)	HPLC	yield 23.30 mg/g	22
chamomile components	chamomile flowers	pressure: 200 atm temperature: 45˚C time: static 2 min. dynamic 30 min. flow rate: 1l/min restrictor: 70˚C modifier: 5% MeOH trap: EtOH	GC-MS, HPLC	recovery 14.6-187.7%	23
carvone and limonene	caraway seed (*Carum carvi* L.)	pressure: 123 atm temperature: 32˚C time: dynamic < 45 min. flow rate: 4 kg/hr	GC		24
α- and β-acids volatiles	cones and leaves of hop (*Humulus lupulus* L)	pressure: 197 atm temperature: 40˚C time: 6 hr	HPLC, GC		25
steviol glycosides	*Stevia rebaudiana*	pressure: 368 atm temperature: 40˚C static: 10 min. dynamic: 80 min. modifier: 20% MeOH added at 40 min trap: organic solvent, at room temperature	CE	recovery 88 %	26
taxicin (to synthesize anti-cancer drugs)	needles of the English yew tree, *Taxus baccata*	pressure: 400 atm temperature: 50˚C dynamic: 100 min. modifier: 10% MeOH	SFC, NMR	yield 666 mg/kg	27
schisandrol A, schisandrol B, schisandrin A, schisadrin B, schisadrin C	*S. chinensis* fruits	pressure: 336 atm temperature: 60˚C dynamic: 100 min. modifier: 10% MeOH	HPLC	yield 0.58 mg/100mg 0.164 mg/100mg 0.134 mg/100mg 0.597 mg/100mg 0.113 mg/100mg	28
hyoscyamine scopolamine salts	Scopolia *japonica* Maxim	pressure: 336 atm temperature: 60˚C static: 15 min. flow rate: 0.8-1.2 mL/min dynamic: 150 mL fluid modifier: 10% dimethylamine trap: MeOH	GC-FID	yield 6.24 mg/g 0.24 mg/g	29
sesquiterpene lactone parthenolide	feverfew (*Tanacetum parthenium*)	pressure: 247 atm temperature: 45˚C flow rate: 0.85 mL/min modifier: 4%MeOH or CH_3CN trap: flask (-170˚C)	GC	yield 0.16 mg/g	30
flavanones xanthones	root of *Maclura pomifera*	fluid: DCM pressure: 136 atm temperature: 100˚C static: 5 min (equilibrium)	HPLC		31

Table 1. Continued

Useful ingredients	Herb	SFE parameters	Analytical method	Analytical figure of merits	Reference
		+ 5 min. dynamic: 90 sec purge (3 cycles, total time 35min.) fluid: CO_2 pressure: 400 atm temperature: 80˚C static: 15 min. dynamic: 30 min. modifier: 20% MeOH flow rate: 1.5 mL/min trap: DCM			
essential oil (frenchone and camphor)	lavender flowers	pressure: 79 atm temperature: 35˚C passing time: 4 s particle size: 1500 μm	GC-FID	relative yield: 82.8%	32

SFC: Supercritical Fluid Chromatography.
FID: Flame Ionization Detection.
HPLC: High Performance Liquid Chromatography.
ESI: Electrospray Ionization.
NMR: Nuclear Magnetic Resonance.
ELSD: Evaporative Light Scattering Detection.
GC: Gas Chromatography.
MS: Mass Spectrometry.
CE: Capillary Electrophoresis.

Table 2. SFE of useful ingredients from plants

Useful ingredients	Plant	SFE parameters	Analytical method	Analytical figure of merits	Reference
volatile Flavor compounds	roasted peanut	pressure: 95 atm temperature: 50˚C time: static10 min. dynamic 10 min. density: 0.35 g/mL trap: silica particles with a hydrophilic coating	GC-MS	content 2.07E-04 – 112E+00 (µg/g)	33
volatile oil antioxidants (p-Cymen-7-ol)	*Eucalyptus camaldulensis* var. *brevirostris* leaves	pressure: 197 atm temperature: 50˚C time: 2 hr flow rate: 2 mL/min trap: EtOH (ice bath)	GC/MS	content 2.25 %	34
essential oil flavonoids (apigenin-7-glucoside, apigenin)	chamomile flowers	pressure: 90 or 200 atm temperature: 40 or 45˚C time: static 2 min. dynamic 30 min. modifier: 5% MeOH flow rate: 1 L/min	GC/MS、RP-HPLC	recovery 14.6-19.5 %	35
fatty acid sterols	plant tissue	pressure: 395 atm temperature: 40˚C time: dynamic 20 min. flow rate: 2 mL/min fluid: $CHClF_2$ (Freon-22) or CO_2 modifier: 10% MeOH trap: 2 mL DCM	GC-FID, GC/MS	content 9342 µg/g 1195 µg/g	36
rosemary antioxidant	preprocessed rosemary plants	two-stage extraction flow rate: 3-4 mL/min first stage pressure: 99 atm temperature: 40˚C time: static 5 min. dynamic 30 min. second stage pressure: 395 atm temperature: 60˚C time: static 5 min.	GC/MS	content first stage 1-1.5% second stage 1-1.8%	37

Table 2. Continued

Useful ingredients	Plant	SFE parameters	Analytical method	Analytical figure of merits	Reference
		dynamic 30 min. low-temperature trap			
antioxidant and essential oil	rosemary leaves	two traps to collect pressure: 296-345 atm temperature: 40-60˚C modifier: 2% EtOH	LC/MS		38
antioxidants	rosemary leaves	pressure: 378 atm temperature: 120˚C flow rate: 4 mL/min static: 0 min. dynamic: 20 min. trap: ODS	HPLC, ESI-MS	carnosic acid SC-CO_2 extraction: 35.7 mg/g acetone extraction: 26.2 mg/g MeOH extraction : 15.9 mg/g hexane extraction: 1.90 mg/g DCM extraction: 7.9 mg/g	39
polyphenolic compounds	grape seeds	pressure: near critical pressure temperature: 55˚C density: 0.95 g/mL restrictor: 50˚C flow rate: 1 mL/min modifier: 0.25 mL MeOH when static; 10% MeOH when dynamic time: static 20 min. dynamic 20 g CO_2 trap: Isolute C_{18} 35˚C,	HPLC-UV	recovery SFE: 77.6% LSE: 65.6% SALSE: 63.0%	40
glycosides	grape	matrix: sand density: 0.95 g/mL temperature: 40˚C flow rate: 1.5 mL/min modifier: MeOH 20% time: static 15 min. dynamic 20 min. restrictor: 50˚C trap: H_2O, 8 mL, 30˚C	GC	94.1 %	41
azadirachtin A	neem seed kernels	pressure: 296 atm temperature: 40˚C	HPLC, LC-MS	2291 mg/kg	42
essential oil	lavender	extraction pressure: 89 atm temperature: 48˚C time: 150 min. flow rate: 0.8 kg/hr separation 80 atm, -10˚C; 25 atm, 0˚C	GC-MS	yield 34.7%	43
pyrrolizidine alkaloids	*Sensecio* species	pressure: 148 atm temperature: 55˚C density: 0.65 g/mL modifier: MeOH 800 μL	GC	yield 2.87-0.10 mg/g	44
review of flavor and fragrance					45
michellamines A and B (anti-HIVcytopathic alkaloids)	*Ancistrocladus korupensis* leaves	pre-extraction with 10% MeOH to filter impurities, increase to 25 % MeOH, time: dynamic 60 min. trap: 2-3 mL MeOH	HPLC	recovery MAA 96% MAB 130.7%	46
identification of 118 compounds	*Angelica archangelica* L. root oil	pressure: 118 atm temperature: 40˚C time : static 1 hr dynamic 2 hr flow rate: 0.5 kg/hr	capillary GC-MS		47

Table 2. Continued

Useful ingredients	Plant	SFE parameters	Analytical method	Analytical figure of merits	Reference
friedelan-3-ol and friedelin	leaves of *Maytenus aquifolium Martius*	modifier: EtOH			48
laurel essential oil	laurel leaves	sub-critical water pressure: 49 atm temperature: 150˚C static: 15 min. time: dynamic 20 hr flow rate: 2 mL/min	liquid extraction followed by GC-MS		49
		sub-critical DCM pressure: 25 atm temperature: 80˚C time: static 15 min. dynamic 20 min. flow rate: 2 mL/min	GC-MS		
α-carotene and β-carotene	freeze-dry Carrot tissue	pressure: 300 atm temperature: 50˚C modifier: 10% EtOH flow rate: 0.5 mL/min trap: 10 mL hexane/acetone (9:1) containing 0.005 % BHT	HPLC	< 65 mg/g for α-carotene > 63 mg/g for β-carotene	50
essential oil	*Eucalyptus camaldulensis* var. *brevirostris*	pressure: 197 atm temperature: 50˚C modifier: none flow rate: 2 mL/min trap: EtOH (ice bath)	GC-MS	yield 0.29 g/100g	51
phenol compounds	olive leaves	pressure: 330 atm temperature: 100˚C density: 0.7 g/mL modifier: 10 % MeOH flow rate: 2 mL/min time: dynamic 140 min. trap: MeOH or hexane	ESI-MS	3.4 mg/g	52
marjoram essential oil	marjoram leaves	sub-critical water pressure: 49 atm temperature: 150˚C flow rate: 2 mL/min time: dynamic 15 min.	GC-FID		53

RP: Reverse Phase.

from eight studies are listed in Table 3[12,13, 23, 26, 28, 31, 39, 54]. The extraction efficiency of SFE is clearly better than that of conventional extraction means based on the limited data set. More research and experimental data are needed to warrant this presumption. We therefore suggest that SFE is a better choice, based on extraction efficiency alone, to extract the useful ingredients from herb and plant matrices.

Sfe of Residual Pesticides from Herbs and Plants

Increasing agricultural production is generally done with the use of pesticides. The residual pesticides in herbs and food plants constitute a potential risk to consumers. This concern stimulated the regulation of pesticides in herbs and food plants to control their levels through maximum residue levels. To meet this trend, certain manufacturers have implemented analytical procedures to determine residual pesticides in herbs as part of their QA/QC system[55-59]. The intrinsic advantages of pre-concentration effect, cleanness and safety, quantitation capability, expeditiousness and simplicity with supercritical fluids over organic solvents for treatment of solid samples are well known. Several drawbacks, including the difficulty of extracting polar analytes owing to the non-polar character of the CO_2 used, the different recoveries obtained from spiked and natural samples, and the frequent need for clean-up steps after extraction, limit the widespread use of SFE and are discussed in a recent review paper[60].

Despite these drawbacks, the use of SFE for pesticide extraction from herbs and plants is still attractive as the application examples shown in Table 4[4,5,61~73]. The analytes include organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs), organonitrogenous pesticides (ONPs), and pyrethroid pesticides. The corresponding SFE parameters, analytical method, recovery (or yield) and reference are also listed. Detailed inspection of these applications reveals that most applications extract pesticide residues at a pressure greater than 200 atm and at a temperature between 40 and 60˚C. Methanol is the most commonly used modifier. The extraction time is usually 15 min for static extraction and less

Table 3. Comparison of ingredient extracting efficiency between SFE and conventional method

Useful ingredients	Averaged recovery	Reference
artemisinin and artemisinic acid	0.63 with SFE 0.52 with liquid solid extraction	12
artemisinic acid from *Artemisia annua* L.	0.47 with SFE 0.45 with liquid extraction 0.45 with sonication	13
chamomile extracts	6.06 with SFE 6.12 with steam distillation	23
stevioside in the *Stevia rebaudiana* leaves	13.7 ± 5.8 with sub-critical fluid extraction 13.1 ± 9.3 with liquid extraction	26
liganans of *Schisandra chinensis*	0.318 with SFE 0.384 with MeOH extraction 0.307 with $CHCl_3$-MeOH (2:1) 0.300 with n-hexane 0.297 with petroleum ether	28
flavanones and xanthones from the osage orange tree root bark	0.370 (± 3.23 % RSD) with SFE 0.373 (± 4.24 % RSD) with pressurized DCM fluid	31
carnosic acid	35.7 (± 1.6 % RSD) with SFE 26.2 (± 1.5 % RSD) with acetone 15.9 (± 1.3 % RSD) with MeOH 1.90 (± 0.08% RSD) with hexane 7.9 (± 1.1% RSD) with DCM	39
Scutellariae Radix extracts	49.47 with SFE using MeOH-H_2O (7:3) modifier 11.37 with SFE using MeOH modifier (CO_2: modifider=20:3) 10.77 with percolation overnight in MeOH 40.5 with ultrasonic shaking in MeOH-H_2O (7:3) 13.1 with MeOH extraction 7.8 with EtOH extraction	54

Table 4. SFE of pesticide residues in herb and plant matrices

Analytes	Matrix	SFE parameters	Analytical method	Analytical figure of merits	Reference
OCPs	vegetable samples	pressure : 300 atm temperature : 50˚C modifier : 200 μL MeOH time : static 1 min dynamic 15 mL CO_2 trap : 3 mL ethyl acetate	GC/FPD, GC/ECD, HPLC/DAD	except for imidaclorprid, recoveries were greater than 80%	61
92 pesticides OCPs OPPs ONPs pyrethroid pesticides	fortified apple matrices	pressure :187 atm temperature : 45˚C flow rate : 2.5 mL/min time : static 1 min dynamic 10 min trap : ODS, 45˚C nozzle temp : 60˚C washing solvent : Hexane-acetone	GC-TSD GC-ECD HPLC-DAD	organochlorine derivative pesticides : 80-131% OCP : 52-76% OPP and ONP : 72-128% pyrethroid pesticides : 84-90%	62
pentachlorophenol	wood	pressure : 300 atm temperature: 50˚C time static 10 min dynamic 25 min, CO_2 30 mL trap : ice-cooled dual-chamber trapping vials with 15 mL of light petroleum.	GC-ECD	recovery : 88-98%(inert matrix)	63
OCPs	garlic	pressure : 299 atm temperature : 40˚C CO_2 = 25 mL time : static 1 min 5g sample with 2×1g $MgSO_4$ on the top as well as at the bottom of the cartridge. trap : hexane	GC-ECD	recovery : 85-110% RSD 3.9-7.2%	64

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Table 4. Continued

Analytes	Matrix	SFE parameters	Analytical method	Analytical figure of merits	Reference
OCPs	Chinese herb medicine	pressure : 250 atm temperature : 50˚C time : static 5 min, dynamic 20 min pure CO_2 2g Florisil/0.1g sample	GC-ECD	recovery : 78-121% reproducibility : 5-31%	5
DuPont herbicides	pea leaves	pressure : variable temperature : 45˚C modifier : water:MeOH (50:50) time : variable			65
thiocarbamate pesticide (methomyl methiocarb eptam)	apples	pressure : 345 atm temperature : 50˚C flow rate : 2 mL/min time : static 2 min, dynamic 30 min tandem trapping: stainless steel beads (-30˚C) + MeOH trap (13˚C)	HPLC-UV HPLC-SCD GC-FID	recoveries : 63.0-84.3% 71.4-83.3% 0-47.6%	66
fusarium mycotoxins	cereals	pressure : 314 atm temperature : 40˚C time : static 30 min dynamic 15 min flow rate : 2 mL/min modifier : 500 μL MeOH (before SFE) + 3% MeOH	GC-ECD HPLC-FLD		67
trichothecene mycotoxins	wheat	pressure : 314 atm temperature : 40˚C density: 0.92 g/mL trap : silica (85˚C)	HPLC-DAD GC-ECD	recovery: 90.1 ± 10.7% (spiked samples) 53.0 ± 3.2% (naturally contaminated samples)	68
2,4-dichlorophenol	food crop tissue	pressure :204 atm for straw matrices, 238 atm for seed matrices temperature : 40˚C time : 45 min flow rate : 170-270 mL/min (gaseous) trap : dual collection vessel (isocatane/aqueous KOH)	HPLC-EC	spiked 0.1-1 ppm recovery : SFE : 18-110% SDE : 49-89%	69
carbendazim, benomyl, thiophanate methyl, 2, 4-dichlorophenoxyacetic acid	fruits and vegetables	pressure : 329 atm temperature : 55˚C density : 0.89 g/mL time : static 2.5 min, dynamic 25 min flow rate : 1.8 mL/min trap : ODS (10˚C)	GC-MS HPLC		70
carbendazim	lettuce sample	density : 0.75g/mL temperature : 50˚C time : dynamic 25 min modifier :50 μL MeOH flow rate : 1.8 mL/min trap : 550-650 μm stainless steel balls (10˚C)	HPLC-UV	SFE : 53.7-98.4% LLE : 94.7-97.3% LLE works better for high concentration sample (>6mg/Kg) SFE works better for low concentration sample, good reproducibility	71
OPPs	wheat flour	pressure :204 atm temperature : 60˚C time : static 20 min dynamic 40 min flow rate : 0.7~1.4 mL/min	GC-NPD	SFE recovery similar to LLE	72
OPPs	rice	pressure : 306 atm temperature : 45˚C	GC-Atomic emission detector	recovery :118-68% better than solvent	37

Table 4. Continued

Analytes	Matrix	SFE parameters	Analytical method	Analytical figure of merits	Reference
		modifier : 5% (v/v) MeOH density=0.914 g/cm^3 flow rate=1.0-1.5 mL/min		extraction	
OCPs: Organochlorine Pesticides.		OPPs: Organophosphorus Pesticides.		ONPs: Organonitrogenous Pesticides.	
FPD: Flame Photometric Detection.		ECD: Electron Capture Detection.		DAD: Diode Array Detection.	
TSD: Thermoionic Specific Detection.		UV: Ultra Violet.		SCD: Sulfur Chemiluminescence Detection.	
FLD: Fluorescence Detection.		FID: Flame Ionization Detection.		EC: Electrochemical Detection.	
NPD: Nitrogen/Phosphorous Detection.					

Table 5. Comparison of pesticide extracting efficiency between SFE and conventional method

Pesticide and matrix	Averaged recovery	Reference
OPPs in the wheat flour certified reference material	1.128 (±10.3% RSD) with SFE 1.107 (±9.6% RSD) with solvent	72
OPPs in the real wheat flour	0.0031 (±6.607% RSD) with SFE 0.0032 (±5.747% RSD) with SFE	72
OPPs in rice	0.327 with SFE 0.323 with MeOH soaking	73
2,4-dichlorophenol in spiked control food crop tissues	65 (±8% RSD) with SFE 71 (±7% RSD) with steam distillation	69
2,4-dichlorophenol in field-treated food crop tissues	0.42 (±16% RSD) with SFE, LOD:0.12 ppm 0.58 (±12 % RSD) with SDE, LOD:0.03 ppm	69

Table 6. Comparison of experimental parameters for SFE of OCPs from different matrices

Sample	Sample amount (g)	Extracting Pressure (atm)	Modifier (mL)	Static extracting time (min)	Dynamic extracting time (min)	Extracting temperature (˚C)	Clean-up trap	Eluting solvent (mL)
sulfur containing Soil	~ 2.0	250	acetone 0.1	5	20	50	1.5-g activated Cu (or $AgNO_3$ loaded silica)	n-hexane 6
mussel	~ 0.3	250	none	5	20	50	2.0-g Florisil	n-hexane 12
Chinese herbal medicine	~ 0.1	250	none	5	20	50	0.1-g Florisil	n-hexane 12

than 30 min for dynamic extraction.

A comparison of pesticide extracting efficiency between SFE and conventional method is listed in Table 5[69, 72, 73]. Based on the recovery and relative standard deviation, SFE does not appear to be significantly better than the traditional extraction method. These results do not provide a systematic relationship between the SFE experimental parameters and the targeted analytes. Table 6 lists the results of our SFE studies of OCPs in different samples including soil[74], mussel[75], and CHM[5] matrices and indicates that the SFE parameters are more targeted compounds oriented, rather than matrix oriented. The nature of the clean-up trap depends more on the matrix where most of the interfering species come from.

From the literature review of the SFE application examples, SFE has proven to be a practical and powerful method for the extraction of useful ingredients and pesticide residues from natural products and food plants. Considering the medical purpose of CHM and the matrix similarity between CHM and natural products or food plants, the use of SFE CO_2 to replace traditional organic solvents is well justified and promising. The coupling of sub-critical H_2O and supercritical CO_2 is also promising for the extraction of medium polar and non-polar compounds. The dual role of extracting useful ingredients and harmful pesticide residues using the same extraction medium makes SFE even more promising. A systematic and effective means to reach the optimal extraction conditions is yet to come, such as a statistical experimental design[32, 40]. Careful integration of laboratory SFE results into design and factory production is beneficial in ensuring the successful use of SFE in CHM.

ACKNOWLEDGEMENTS

The authors are grateful to the Committee of Chinese Medicine and Pharmacy, Department of Health, and the National Science Council, ROC for supporting the supercritical fluid extraction work.

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超臨界流體於中草藥之應用－由製備到分析

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（收稿：July 20, 2000；接受：November 15, 2000）

摘　要

本文回顧文獻中超臨界流體於中草藥的萃取及分析之應用，預料應用超臨界流體於中草藥產品之製備會愈來愈廣泛。文中並逐一探討有效成分之製備及有害成分之分析的應用實例。超臨界二氧化碳流體具有多種優點，有取代傳統萃取溶劑的趨勢，配合次臨界水的使用，可應用於更多種類的中草藥，同時具有萃取有效成分及去除有害成分的雙重功效。若能有效的整合實驗室結果應用於中草藥產品量產工廠的設計及生產，將有助於使超臨界流體萃取成功的應用於中草藥。

關鍵詞：中草藥，超臨界流體萃取，有效成分，農藥殘留