Review

The recent progress of solvent sublation

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ABSTRACT

Solvent sublation is a kind of adsorptive bubble separation technique in which the surface-active (or hydrophobic) compounds in aqueous phase are adsorbed on the bubble surfaces of an ascending gas stream and then collected in an organic layer placed on top of the aqueous phase. The technique has many advantages, such as high separation efficiency, high concentration coefficient, low dosage of organic solvent, soft separation process, and simple operation. Thus, this technique has been widely applied in many fields. The present article reviews solvent sublation's theoretical research and some applications in the last 10 years, and gives the development trend in the future.

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Contents

1. Introduction

Solvent sublation (SS), a non-foaming technique, was originally introduced by Sebba [1] as an improved method for the ion flotation in 1962. In this special adsorptive bubble separation technique, some organic solvent placed on the top of aqueous phase is used to collect the sublate adsorbed on the bubble surfaces of an ascending gas stream. This method, with its advantages of simultaneous separation and concentration, has recently attracted much attention in many fields.

To date, a few valuable reviews have been published since the adsorptive bubble separation technique is studied extensively. In Lemlich's book, *Adsorptive Bubble Separation Techniques*, there was an excellent review on solvent sublation by Karger [2]. Wilson et al. also evaluated the prospect of solvent sublation for the removal of some organic compounds from aqueous phase in a general review [3] and two books [4,5]. Another outstanding recent review is by Lü and Zhu [6], who gave a complete description of solvent sublation theory and its applications from 1962 to 1999. Since the literatures on the new theoretical research and some interesting applications of solvent sublation were published after 1999, the recent development will be thoroughly reviewed in this paper.

Based on the previous reports and recent research, we outline the main advantages of solvent sublation here:

(1) *High separation efficiency*. Although the knowledge of liquid–liquid extraction (LLE) can be applied to develop efficient solvent sublation procedures, solvent sublation has practical and theoretical advantages over liquid–liquid extraction. In liquid–liquid extraction the quantity of substance transferred from aqueous phase to organic phase is determined and limited by an equilibrium constant. In solvent sublation,

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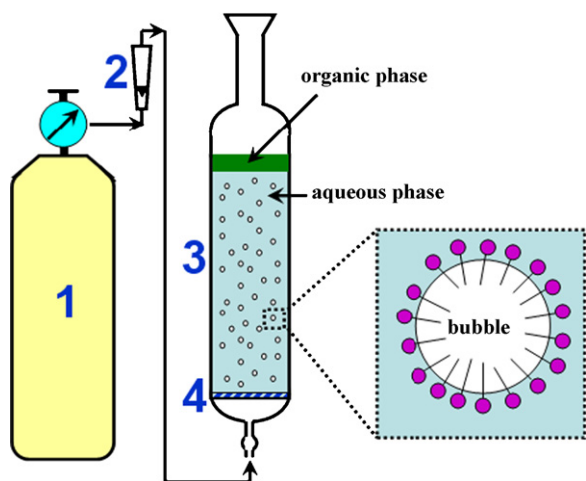*E-mail address:* donghr@mail.buct.edu.cn (H.-r. Dong).

Fig. 1. Solvent sublation apparatus. (1) Nitrogen cylinder; (2) rotameter; (3) flotation cell; (4) sintered glass disk (G$_4$ porosity).

this equilibrium state cannot be established in the bulk of the system but only at the aqueous–organic interface, because the mass transfer process is greatly strengthened by the bubble mass transfer. As a result, the separation efficiency of trace substances can eventually reach 100%.

(2) *High concentration coefficient.* Due to the capability of processing large volumes of aqueous samples, the concentration coefficient of solvent sublation can easily exceed ratios of 100:1. Different from the previous applications of solvent sublation, the concentration coefficient of the recent applications can reach 200:1, thus making the technique has great potential applications for the analysis of trace substances in natural, residual and marine waters.

(3) *Low dosage of organic solvent.* Another benefit of the high concentration coefficient is the minimization of organic solvent consumption. Therefore, solvent sublation is an environment-friendly and money-saving technique, and a safe environment can be created for lab workers.

(4) *Soft separation process.* As an improved method of liquid–liquid extraction, in solvent sublation the mass transfer process is greatly strengthened by the unidirectional mass transfer of bubbles. Usually the gas stream of solvent subaltion is quite mild, and a sublate can dissolve into the upper organic layer without drastic mixing process between the aqueous and organic phases. So it can maximally avoid the formation of undesirable emulsions, especially for the extraction of surface-active species.

(5) *Simple operation.* As the classical apparatus shows (Fig. 1), the equipments used in solvent sublation are very simple, and all the operator needs to do is to collect the upper organic layer for the sequential analysis or further treatment.

This article mainly reviews the progress of solvent sublation in the recent 10 years. It starts with some new theoretical research of solvent sublation, and then the attention is devoted to some interesting new applications. Furthermore, some new theoretical discussion is also presented here for the first time.

2. Theoretical research

During the period from 1962 to 1999, Sebba [1], Karger [2], Wilson and co-workers [7–10], Valsaraj and co-workers [11–17], Palagyi and Braun [18–20], etc., respectively studied the mechanism of solvent sublation, and their works were summarized in the previous reviews [1,2,6]. In the last 10 years, only two groups, Lü's group and Dong's group published their theoretical research results, including not only the kinetics and thermodynamics studies but also the theoretical models.

2.1. Kinetics and thermodynamics

Usually the separation process of solvent sublation obeys the first order kinetics equation in the dilute solution system (the sublate concentration is lower than CMC). Recently, Lü's group researched a serial separation behavior of surfactants (or surfactant–dye complexes) by solvent sublation [21–29]. All the separation systems of solvent sublation obey the first order kinetics equation with different air flow rate and different temperature, such as hexadecylpyridinium chloride (HPC) and dodecylbenzenesulfonic acid (LBS) (Fig. 2 [21]).

At the same time, Lü et al. also calculated the apparent activation energy of solvent sublation in different separation systems by the related kinetics behaviors. They considered that the solvent sublation process can be regarded similar to a chemical reaction, i.e. the substance cannot be sublated unless it can overcome the energy peak of the water-film [21].

In the separation process of solvent sublation, the rate is followed by

$$-\frac{dc}{dt} = kc^n \tag{1}$$

where c is the sublate concentration in the aqueous phase, k is the apparent rate constant and n is the order of the solvent sublation. Upon the analysis of the previous reports, it is obvious that the kinetics of the solvent sublation process was obedient to the first
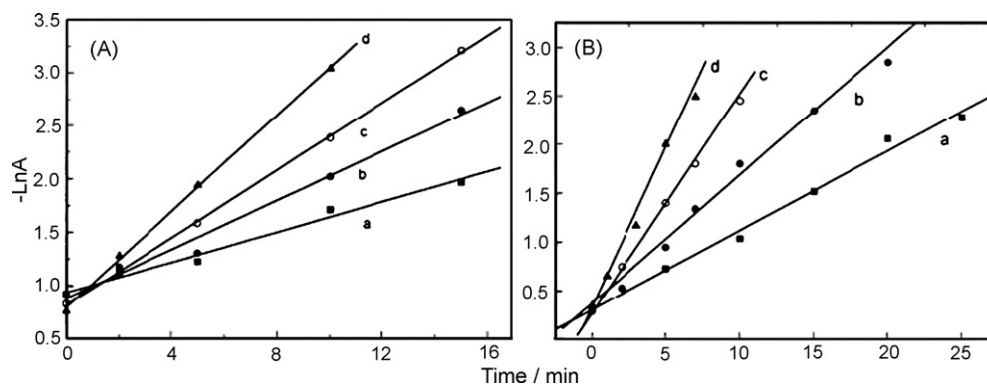

Fig. 2. Curve of ln$A$ against time, air as the gas in the sublation column. (A) HPC: a, 35; b, 75; c, 125; d, 250 ml/min. (B) LBS: a, 25; b, 40; c, 70; d, 115 ml/min.

Table 1
Solvent sublation apparent activation energies (E_s) of different sublates.[a]

Sublate	E_s	Separation conditions	Ref.
LBS[b]	8.11 kJ/mol	LBS solution 500 ml (7.75×10^{-5} mol/l), isopentanol 10 ml	[21]
BB–HPC[c]	4.77 kJ/mol	HPC/BB = 2:1 (mole ratio), air flow rate = 75 ml/min, 1.0×10^{-5} mol/l BB, solution 350 ml, isopentanol 5 ml	[22]
MV–DBS[d]	8.19 kJ/mol	MV/DBS = 1:1 (mole ratio), air flow rate = 65 ml/min, MV solution 400 ml (1.58×10^{-5} mol/l), 2-pentanol 10 ml	[23]
$[(C_{12}H_8N_2)_3Fe^{2+}]$–DLS[e]	12.18 kJ/mol	$[(C_{12}H_8N_2)_3Fe^{2+}]$/DLS = 1:20 (mole ratio), air flow rate = 65 ml/min, pH 7.0, $[(C_{12}H_8N_2)_3Fe^{2+}]$ solution 500 ml (2.3×10^{-5} mol/l), isopentanol 10 ml	[24]
IC–CBA[f]	1.3 kJ/mol	IC/CBA = 1:2 (mole ratio), air flow rate = 75 ml/min, natural pH value, IC solution 400 ml (2.5×10^{-5} mol/l), 2-octanol 5 ml	[25,26]
HA–HPC[g]	9.48 kJ/mol	Air flow rate = 75 ml/min, pH 6, 50 mg/l HA, HPC solution 500 ml (40 mg/l), isopentanol 5 ml	[27]
Ni^{2+} complex[h]	8.99 kJ/mol	SDS/Ni = 20:1 (mole ratio), air flow rate = 75 ml/min, pH 11, Ni-diacetyl-dioxime solution 250 ml (6.8×10^{-5} mol/l), isopentanol 10 ml	[28]
BG–HPC[i]	1.3 kJ/mol	BG/HPC = 1:1.25 (mole ratio), air flow rate = 75 ml/min, pH 3–4, BG solution 300 ml (5.0×10^{-5} mol/l), isopentanol 5 ml	[29]

[a] All the experiments were carried out in a similar separation apparatus [21].
[b] Dodecylbenzenesulfonic acid.
[c] Bromophenol blue-hexadecyl pyridium chloride complex.
[d] Methyl violet-sodium dodecylbenzensulfonate complex.
[e] $[(C_{12}H_8N_2)_3Fe^{2+}]$-sodium dodecyl-phrate complex.
[f] Indigo carmine-cetyltrimethyl ammonium bromide complex.
[g] Humic acids-hexadecylpyridium chloride complex.
[h] Ni^{2+}-diacetyldioxime-sodium dodecylbenzen-sulphonic complex.
[i] Bromocresol green-hexadecylpyridium chloride complex.

order kinetics equation.

$$-\frac{dc}{dt} = kc \qquad (2)$$

So the Arrhenius equation can be used to describe the separation process of solvent sublation,

$$\ln k = -\frac{E_s}{RT} + B \qquad (3)$$

where k is the apparent rate constant, R is the gas constant, B is the integrate constant, E_s is the apparent activation energy of solvent sublation. The relationship of $\ln k$ and $1/T$ is linear, and the value of the apparent activation energy can be calculated from the slope of the curve [22,23,25,27].

We can see that the apparent activation energy can be used as a characteristic parameter to describe the solvent sublation process. In fact, the separation system and the separation parameters have decisive effects on the apparent activation energy. Table 1 shows the apparent activation energies of different sublates.

2.2. Theoretical models

Mathematical model is a good way to describe and explain the mechanism of solvent subaltion. The earlier theoretical models of solvent sublation were established by Wilson and co-workers [5,7–9]. They built the mathematical model of the aqueous solution on the assumptions of Langmuir adsorption transport and ion equilibrium. But the theoretical results showed discrepancies from the experimental results. In 1991, Valsaraj and Thibodeaux [12,13] investigated the mechanism of neutral pentachlorophenol (PCP) and PCP–hexadecyltrimethyl ammonium bromide complex in solvent subaltion, and gave the complete mathematical model of solvent subaltion for the first time. In this model, two predominated processes mentioned by Karger [2] were used: (1) transport within and on the surface of the bubbles; (2) a diffusive transport between the phases driven by a concentration gradient. Furthermore, Valsaraj and Thibodeaux [12] considered two additional processes in the solvent subaltion process: a thin film of water is dragged into the solvent phase and is then returned as water droplets.

Based on the principle and the complete mathematical model, Lü and Zhu [30] used a simplified mathematical model (without

Herry's constant) to describe the solvent sublation of surfactants (HPC and LBS). The simplified mathematical model is shown as follows:

$$V_w \frac{dC_w}{dt} = -Q_a \left(\frac{3}{a}K_a + \frac{3}{a}d_i\right) C_w$$
$$-\pi r_c^2 K_1 \left(C_w - \frac{C_o}{K_{ow}}\right) + Q_a \frac{3}{a}d_i \frac{C_o}{K_{ow}} \qquad (4)$$

where "–" represents the process of the sublate transfer from the aqueous phase to the organic phase; V_w, the volume of aqueous phase; C_w, the concentration in aqueous phase of the sublate at t; Q_a, gas flow rate at 1 atm; a, bubble radius, which must use the value of bubbles after coalescence when behavior of coalescence exists; K_a, the linear adsorption constant for the sublate between the gas–water interface of the gas bubbles and the aqueous phase; d_i, thickness of aqueous phase layer around the bubbles; r_c, column radius; K_1, aqueous phase mass transfer coefficient; V_o, the volume of organic phase; C_o, organic phase sublate concentration; K_{ow}, sublate partition constant between the organic phase and aqueous phase; t, solvent sublation time.

Using the simplified mathematical model, many parameters of solvent subaltion were analyzed by computer softwares (Mathematic 4.0, Matlab 5.0 and Runge–Kuta method) for the first time. Moreover, the simulation of the mathematical and experimental data was compared with perfect results.

At the same time, the simplified mathematical model (Eq. (4)) was also applied in dye–surfactant complex [26,31] and metal ion complex [24]. Different from the non-volatile monomolecular system, the equilibrium constant of the complex reaction (K_e) was used to correct Eq. (4). The mathematical simulation data showed the effect of K_e can be neglected when it is large enough ($K_e > 1000$) [24].

In the application of the simplified mathematical model, we found that the simplified mathematical model was not very accurate, even some uncorrected assumptions. So our group reported some papers [32,33] for improving the simplified mathematical model.

It is well known that the bubble radius is one of the very key parameters in solvent sublation. According to the analysis of the coalescence behavior of bubbles on water–organic interface, Bi et al. [32] proposed the conception of critical bubble radius (CBR),
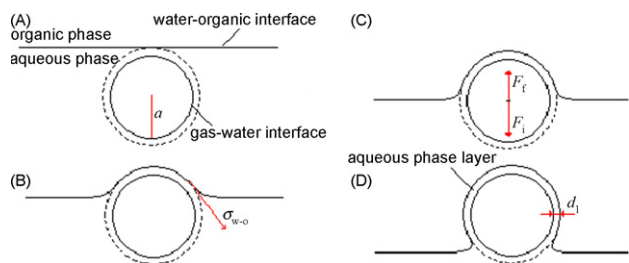
Fig. 3. The process of bubble crossing water–organic interface and entering into organic phase from aqueous phase in the center of sublation column (A → B → C → D). a, Bubble radius; σ_{w-o}, interface tension of water–organic interface; F_f, floatage to bubbles; F_i, the total force to bubbles from interface tension; d_i, thickness of aqueous phase layer around the bubbles.

and proved that the CBR should be adequately considered in the mathematical model of solvent sublation.

The small bubbles cannot cross the water–organic interface immediately, and they should coalesce into large ones in order to overcome the interfacial tension. Fig. 3 shows the process of a bubble crossing the water–organic interface. The stress of the bubble accords Newton mechanics: the bubble is affected by floatage (upwards) and interface tension (downwards). For simplifying the calculation, a hypothesis is given: the edge of the deformation osculates completely with the bubble, and the calculation model is shown in Fig. 4.

According to the change for the stress of rising bubble, the floatage of the bubble can be described as:

$$F_f = \frac{1}{3}(\rho_w - \rho_o)g\pi h^3 - (\rho_w - \rho_o)g\pi a h^2 + \frac{4}{3}\rho_w g\pi a^3 \tag{5}$$

where ρ_w and ρ_o are the density of aqueous phase and the organic phase respectively, and g is gravitational acceleration.

Similarly, the volume and shape of bubble almost does not change in the rising process, so the additional pressure does not change also. According to equation Young–Laplace, the total force to bubbles from interface tension can be described as:

$$F_i = \Delta P \times S = \frac{2\sigma_{w-o}}{a}\pi(2ah - h^2) \tag{6}$$

where ΔP is the additional pressure; σ_{w-o} is the interface tension of water–organic interface.

According to the principle of stress equilibrium, if $F_f \geq F_i$, the bubble can cross the water–organic interface and enter into the organic phase by itself, so the value of CBR can be obtained. At last, the mathematical and experimental data proved that the value of CBR should be used when the bubbles radius in aqueous phase is smaller than the value of CBR. In other words, the reduction of bubble radius cannot accelerate the process of solvent sublation when the bubble radius in aqueous phase is smaller than the value of CBR.
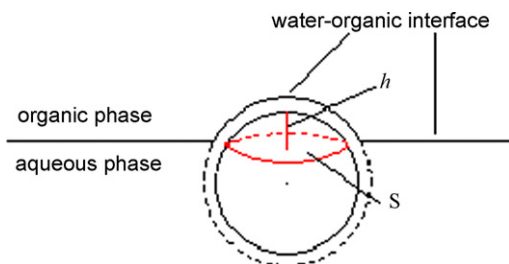

Fig. 4. The perfect model for calculating the F_f and F_i. The h is the height of the part, which has entered into the organic phase; and the S is the sectional area of bubble intercepted by water–organic interface.
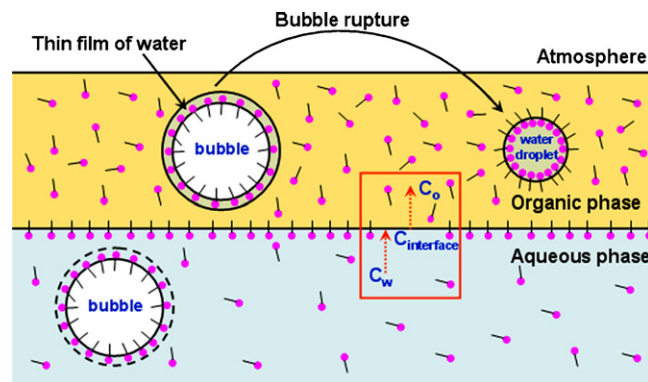

Fig. 5. Mass transfer processes in solvent sublation.

Furthermore, we investigated the additional processes in solvent subaltion: the effect of water droplet [33]. Though the water droplets have very weak influence on the kinetics process [30], it can evidently affect on the thermodynamic equilibrium of solvent subaltion. We described the mass transfer process between organic phase and water droplets, and a new conception, the average area of mass transfer between organic phase and water droplet in the increasing process of a water droplet (S_d), was proposed. Based on the analysis of water droplets, the classical mathematical model was improved as follows:

$$V_w \frac{dC_w}{dt} = -Q_a \left(\frac{3}{a}K_a + \frac{3}{a}d_i\right) C_w - \pi r_c^2 K_1 \left(C_w - \frac{C_o}{K_{ow}}\right)$$
$$+ Q_a \frac{3}{a}d_i \left\{ \left[e^{-(aS_d K_1/3Q_a d_i)} - \frac{V_w}{V_o K_{ow}}(1 - e^{-(aS_d K_1/3Q_a d_i)})\right]\right.$$
$$\left. C_w + (1 - e^{-(aS_d K_1/3Q_a d_i)})\frac{C_{wi} V_w}{V_o K_{ow}} \right\} \tag{7}$$

The simulation results of the new model were compared with the experimental results, and it proved that the new mathematical model can describe the separation process of solvent subaltion more exactly, especially in the thermodynamic equilibrium.

In fact, to improve the classical mathematical model is not enough to accurately describe the separation process of solvent sublation, and it is very difficult to explain the thermodynamic equilibrium. So we proposed a new mechanism for explaining the real process, and it is shown in Fig. 5. In the traditional theory [12,30], the bubble mass transfer and the mass transfer of thin film of water (water droplets) were separated into two individual processes. The previous researchers considered that the sublate adsorbed on water–gas interface can directly dissolve into the organic phase after bubble rupturing. But we can see that the sublate cannot dissolve into the organic phase immediately, it will keep on staying on the water–organic interface of the water droplets (Fig. 5). Then the sublate will enter into the organic phase by a diffusive transport between the organic phases and the water–organic interface, which is driven by a concentration gradient. Obviously, the mass transfer between the organic phase and the water–organic interface in the bubble mass transfer process is very different with the similar process in traditional liquid–liquid extraction (the red rectangle in Fig. 5). Compared with the traditional liquid–liquid extraction, the sublate concentration on the bubble surface is higher than the water–organic interface between the aqueous phase and the organic phase. Furthermore, after bubble rupturing, the bubble surface transforms into the water–organic interface between the water droplets and the organic phase, and the total area of the interface is rapidly reduced. However, the amount of the sublate on the interface is not reduced. Therefore, the sublate concentration on the water–organic interface is greatly

increased, so the separation balance greatly turns to the organic phase.

According to the new principle, the bubble mass transfer process and the mass transfer of thin film of water (water droplets) can be considered one process, and the separation process of solvent subaltion consists of two individual processes: (1) a mass transfer process of bubbles and water droplets; (2) a diffusive transport between the aqueous phase and the organic phase driven by a concentration gradient.

Though the mass transfer process of bubbles and water droplets is very different with the traditional liquid–liquid extraction, its essence is still a liquid–liquid mass transfer process. So the solvent sublation can be considered a special liquid–liquid extraction, which is greatly strengthened by the bubble concentration effect. The bubble concentration effect effectively increases the sublate concentration of the mass transfer interface.

3. Applications

The traditional applications of solvent sublation focus on the removal of organic pollutants and the sample pretreatment for spectrophotometry. In recent 10 years, solvent sublation has been used to separate and concentrate a broad range of compounds with various chemical properties, and it has verified itself as an efficient pretreatment technique for atomic absorption spectrophotometry (AAS), high performance liquid chromatography (HPLC), and gas chromatography (GC).

3.1. Natural products

The most commonly used technique for separating active components from the extract of natural product is liquid–liquid extraction in which low recovery efficiency and the use of organic solvent in large amounts are disturbing. Solvent sublation has solved those problems. In 2004, solvent sublation was first used to separate and concentrate ephedrine and pseudoephedrine from the extract of *Ephedra Grass* [34]. Then, the technique was applied in the separation and concentration of more active components from the extracts of different natural products [35–38]. Compared with liquid–liquid extraction (Table 2), the separation efficiency in solvent sublation is greatly increased, the time required for the separation is effectively shortened, and the consumption of organic solvent is also reduced.

Why can the active components of natural products be separated by solvent sublation? as shown in Fig. 6, these active compounds (such as ephedrine and pseudoephedrine [34], baicalin [35], icariin [36], phytosterone [37], andrographolide [38], magnolol and honokiol [39]) all have a hydrophilic group (hydroxyl or glucosan) and a hydrophobic group (phenyl or alkyl), and they can be adsorbed on the bubble surfaces of an ascending gas stream and then dissolved in the organic solvent placed on the surface of the sample solution. Therefore, they are suitable for solvent sublation.

Solvent sublation cannot only separate and concentrate the target compound, but also pre-purify the extract. In Fig. 7 [38], andrographolide was separated from the herb extract to the organic phase, and the strong polar impurities (the chromatography peaks from 0 to 10 min) were removed at the same time. Based on the advantage, solvent subaltion was used to treat (purify) the extract of *Magnoliae Cortex* for the HPLC analysis of magnolol and honokiol [39].

However, solvent sublation also has some disadvantages. Solvent sublation is not very suitable for high concentration system, and alcohol extract system (the aqueous phase mainly consists of alcohol, thus it is difficult to find a suitable sulabtion solvent), and the purification effect is limited in most case. Nevertheless, separation and concentration of active components from the extracts of natural products is a good attempt of solvent sublation, and it provides a new idea for the related fields.

3.2. Bioseparation and bioengineering

From 2005, solvent sublation started to be applied in bioseparation and bioengineering. We believe it is the most important development of solvent subaltion in recent years. The application not only develops a new applied field, but also develops two new separation modes of solvent sublation: aqueous two-phase flotation (ATPF) and flotation complexation extraction (FCE).

At the beginning, solvent sublation was limited to remove butyl acetate (BA) from the wastewater, which was the waste fermentation broth of penicillin G after extracting with BA as organic extractant. Sun et al. [40,41] compared two adsorptive bubble separation techniques, air stripping and solvent subaltion, for BA recovery from the wastewater. The experimental results showed solvent sublation has better separation efficiency. At the same time, they investigated the theoretical model [42] of BA recovery by solvent sublation. In order to further understand the separation mechanisms and improve the recovery of BA from the wastewater, Sun et al. [43] also studied the effects of emulsion on the separation process of solvent sublation. Based on the separation idea, one-step solvent sublation was used to remove BA from penicillin G fermentation broth during 6-aminnopenicillanic acid production [44].

The experimental results show reduction of BA emulsification in fermentation broth is more effective than removal of BA from wastewater, thus we directly used solvent sublation to separate penicillin G from fermentation broth [45]. The experimental results prove solvent sublation can effectively overcome the emulsification (the BA residual rate was reduced to 0.03 wt%, and it is far lower than common residual rate 1.0 wt% [46]), and improve the distribution ratio, and remove many strong polar compounds. Moreover, the separation conditions of solvent subaltion were very mild (room temperature and pH 3.5), and the separation costs were also reduced. Though the distribution ratio of solvent sublation is higher than liquid–liquid extraction under mild separation conditions [45], the separation efficiency of the one-step solvent subaltion is still very low (48%), not fit for the purpose of massive production in industry. So we used solvent sublation as the mass transfer mode in an aqueous two-phase system for separating and concentrating penicillin G [47]. We named this new technique, which combines solvent sublation with aqueous two-phase extraction, aqueous two-phase flotation (ATPF). In the ATPF system of polyethylene glycol (PEG)/ammonium sulfate, the separation efficiency of penicillin G was more than 95%, and the separation condition (room temperature and pH 6.8) is milder than the traditional solvent subaltion (room temperature and pH 3.5) [45]. In Fig. 8, experiment result comparison [47] shows that the separation efficiency of ATPF is much better than those of solvent sublation and liquid–liquid extraction, and slightly lower than that of aqueous two-phase extraction. However, the distribution ratio ($D = 100$) and concentration coefficient ($\alpha = 18$) of ATPF were better than those of all the other techniques (LLE, $D = 0.008$, $\alpha = 0.008$; SS, $D = 18.5$, $\alpha = 9.6$; ATPE, $D = 97$, $\alpha = 2.9$). Furthermore, the use of PEG replacing toluene, *n*-octanol, and *n*-hexane, etc., is very helpful to protect environment, and also reduces the cost.

Another breakthrough of solvent sublation on the biological application is the successful separation of amino acids. Amino acids are polar organic compounds, they cannot dissolve in any organic solvent, so neither the traditional liquid–liquid extraction nor the classical solvent sublation can be used for separating amino acids from fermentation liquid. Recently, because of the application of di-(2-ethylhexyl) phosphoric acid (D2EHPA) in an emulsion liquid

Table 2
Applications of solvent sublation for separating and concentrating active components from extract of natural products.

| Natural product	Active component	Solvent sublation			Liquid–liquid extraction			Ref.
		E^a (%)	t^b	V_w/V_o	E (%)	t	V_w/V_o	
Ephedra Grass	Ephedrine and pseudoephedrine	92.39	30 min	10	43.85	30 min	1	[34]
Scutellaria Baicalensis Georgi	Baicalin	95.42	30 min	30	$-^c$	–	–	[35]
Epimedium	Icariin	64.4	45 min	10	28.4	–	5	[36]
Achyranthes Bidetata	Total phytosterone	81.41	1.5 h	20	16.53	2.5 h	1	[37]
Herb Andrographis	Andrographolide	94.1	1 h	2	88.7	6 h	10/3	[38]

[a] Separation efficiency.
[b] Separation time.
[c] "–" is represent that the information is not given in the related report.

membrane [48] and the development of complexation extraction of polar organic compounds [49], amino acids can be separated and purified from the fermentation liquid by complexation extraction containing D2EHPA as a carrier [50,51]. In 2008, we first used the mass transfer mode of solvent subaltion in the D2EHPA complexation extraction of amino acids. By the means of the combination of D2EHPA complexation extraction with solvent sublation, we successfully separated L-phenylalanine from fermentation broth [52], and the results show that the distribution ratio is better than the ones in previous reports. We named this improved solvent sublation for flotation complexation extraction (FCE).

The separation process of FCE consists of solvent sublation and complexation extraction, and the complexation reaction is one step of the whole separation process, also it is the most obvious different between FCE and the traditional solvent sublation (the complexation reaction is before the separation process).
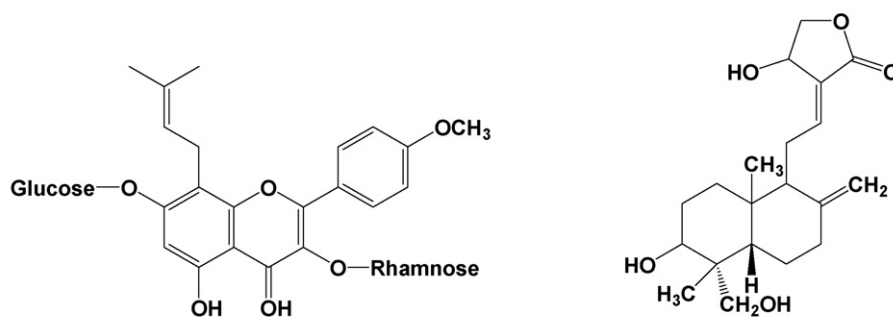
In the separation process of FCE, there are three stages: (1) bubble mass transfer (flotation); (2) reaction between amino acids and
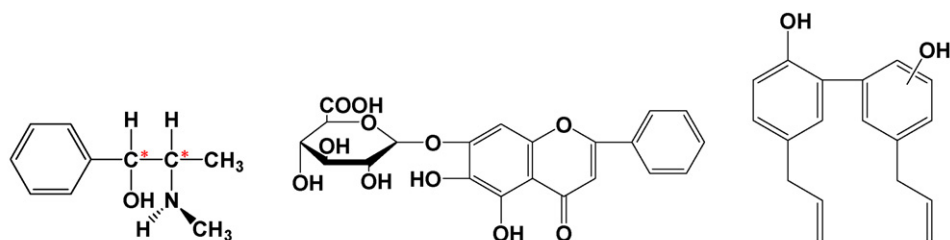
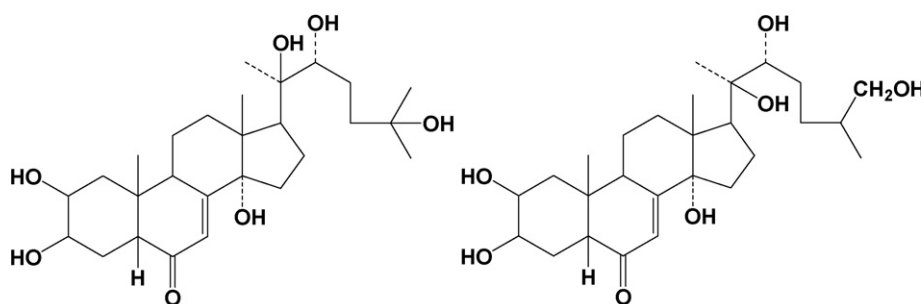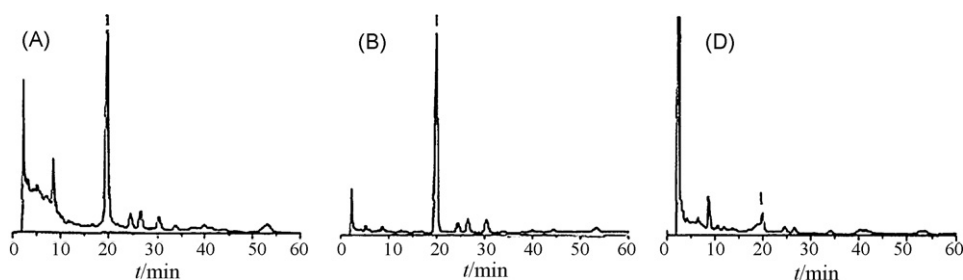Fig. 6. Chemical structures of some active compounds in natural products.

Fig. 7. Chromatograms of herb extract (A), organic phase (B) and aqueous phase (C) after solvent subaltion. The chromatography peak 1 is andrographolide.

D2EHPA (complexation); (3) the complex compound dissolves in organic phase (extraction). Recently, Wu et al. [53,54] improved FCE by using dodecylbenzenesulforic acid as the collector. The improved FCE was used to separate L-lysine [53] and L-arginine [54] from aqueous phase, and the separation efficiency is better than that in FCE. The results prove that some surfactant collectors can strengthen the mass transfer of FCE.

3.3. Analysis of organic compounds

Although solvent sublation can pre-concentrate the target compound from aqueous phase and can be a sample pretreatment technique for instrumental analysis, few papers were published for analyzing organic compounds before 2000 [6], except the trace analysis of ethoxylated non-ionic surfactants by solvent sublation-HPLC [55].

Recently, solvent sublation has been widely applied in the analysis of organic compounds, and is summarized in Table 3.

As shown in Table 3, solvent subaltion can effectively reduce the limit of detection (LOD), and easily handle large volume of aqueous samples in a short time. Generally, the treatment time of solvent sublation with 1 l sample is shorter than 70 min [56–61], is superior to many conventional sample preparation techniques of instrumental analysis (e.g. solid phase extraction and solid phase micro-extraction).

In the pretreatment process, the selection of the sublation solvent is very important, because the different organic solvents may cause some interference in the different detection systems. Usually the anti-interference ability of GC is better than that of HPLC. As shown in Fig. 9 [58], four common organic solvents (toluene, n-octanol, iso-amylalcohol and n-hexane) were used as the sublation solvent for separation and concentration of three pyrethroid pesticides and their determination by HPLC. Obviously, n-hexane and iso-amylalcohol are much better than toluene and

n-octanol, because the former has lower background interference. However, there are still differences between n-hexane and iso-amylalcohol as sublation solvents. The comparison experiments between n-hexane and iso-amylalcohol proved that the background interference of n-hexane is a little less than that of isoamyl alcohol.

Another interesting report is the application of ionic liquid in solvent sublation. Wang et al. [61] substituted 1-butyl-3methylimidazolium hexafluorophosphats ([Bmim]PF$_6$) for the traditional sublation solvents, since ionic liquid (such as [Bmim]PF$_6$) is beneficial to protect environment.

3.4. Analysis of metal ions

Removal and recovery [62,63] of metal ions and their spectrophotometric determination [64,65] are the classical applications of solvent sublation. However, few papers [66] of traditional determination of metal ions were published in the past 10 years. At the end of twentieth century, Kim et al. [67–69] started to use solvent sublation as a pretreatment technique for metal analysis of AAS. Now, more analytical methods of AAS by the virtue of solvent sublation were developed [70–77], as shown in Table 4. Different from the chromatography, the AAS are more easily influenced by the background interference which comes from the sublation solvents. The key is to find a suitable organic solvent for both solvent sublation and AAS. Therefore, the contribution of Kim et al. [67–74,77] was the finding of the suitable organic solvent methylisobutyl ketone (MIBK). Compared with many other organic solvents (e.g. diisopropyl ketone, cyclohexane, benzene, xylene, hexane, octane, etc.), it always has a maximum of absorbance and a minimum of background interference in the AAS analysis. We believe, in the future, solvent sublation can be applied as the pretreatment technique of more instrumental analysis, such as ICP–MS and AES.

3.5. Removal and recovery of organic pollutants

Removal and recovery of organic pollutants, such as dyes [7,78–80], toxic organic solvents [9–11,81–90], organophosphorous pesticides [91], from aqueous phase is the most widely used application of solvent sublation [6]. Recently, many removal methods of organic pollutants by solvent sublation were established. Lü et al. successfully removed dyes (e.g. bromophenol blue [22], methyl violet [23], indigo carmine [25] and bromocresol green [29]), which those complexes with different surfactants, from aqueous phase. Under the optimal conditions, the separation efficiencies of bromophenol blue, methyl violet, indigo carmine and bromocresol green were higher than 95%, 97%, 93% and 99%, respectively. Liu and co-workers [40,41,43,44] removed butyl acetate (BA) from the waste water of penicillin production, and the removal efficiencies were about 60–70%. In the large scale study, Valsaraj and co-worker [92] used a special annular shear sparger for nitrogen gas sparging into the flotation cell. The process was conducted in two-phase continuous and three-phase continuous modes. In the three-phase
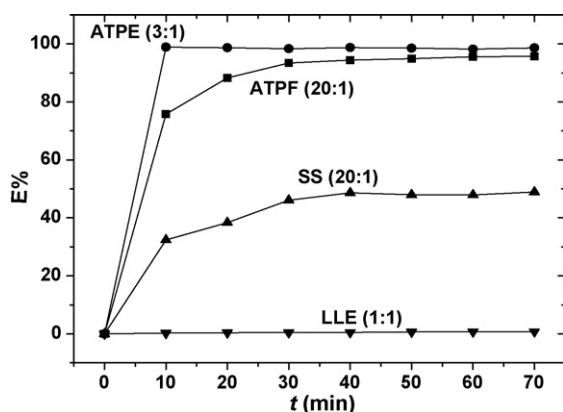

Fig. 8. Comparison experimental results among aqueous two-phase floatation ($V_w/V_o = 20:1$), aqueous two-phase extraction ($V_w/V_o = 3:1$), solvent sublation ($V_w/V_o = 20:1$) and liquid–liquid extraction ($V_w/V_o = 1:1$).

Table 3

Applications of solvent subaltion in instrumental analysis of organic compounds.

Target compounds	Samples	Organic solvent	Preconcentration factor (time)	Determination conditions	LOD	RSD (%)	Recovery (%)	Ref.
Sodium stearate	Sodium aluminate solution	Cyclohexanone	80 (30 min)	GC–FID; column PEG-20M (30 m × 0.32 mm, i.d.); column temperature 190 °C	0.1 mg/l	1.01–1.35	96.9–98.1	[56]
Organophosphorus pesticides	Vegetables	n-Octanol	80 (70 min)	GC–FPD; column HP-1 (30 m × 0.25 mm, i.d.); column temperature 150 °C (2 min), 10 °C/min, 180 °C (2 min), 5 °C/min, 250 °C	1.2–3.5 µg/kg	0.46–4.83	81.3–98.9	[57]
Pyrethroid pesticides	Vegetables	n-Hexane	30 (60 min)	HPLC–UV; column XDB-C18 (5 µm × 150 mm × 4.6 mm); acetonitrile in water (v/v) = 85%; 215 nm; 1.0 ml/min	1.4–4.2 µg/kg	1.70–6.19	85.7–110	[58]
Phthalate esters	River water	n-Hexane	100 (70 min)	HPLC–UV; column XDB-C18 (5 µm × 150 mm × 4.6 mm); acetonitrile in water (v/v) = 60%, 2%/min, 100%; 224 nm; 1.0 ml/min	0.001–0.225 µg/l	2.63–9.71	77–120	[59]
Pyrethroid pesticides	River water	n-Hexane	100 (60 min)	HPLC–UV; column XDB-C18 (5 µm × 150 mm × 4.6 mm); acetonitrile in water (v/v) = 60% (0–15 min), 75% (15–16 min), 1.5%/min, 96%; 215 nm; 1.0 ml/min	0.03–1.80 µg/l	0.78–8.06	89–112	[60]
Tereacyclines	Pond water and river water	[Bmim]PF$_6$[a] in ethyl acetate	20 (50 min)	UV; 389 nm for La(III)-tereacyclines complex	0.3 µg/l	3.0–4.3	96.8–96.7	[61]

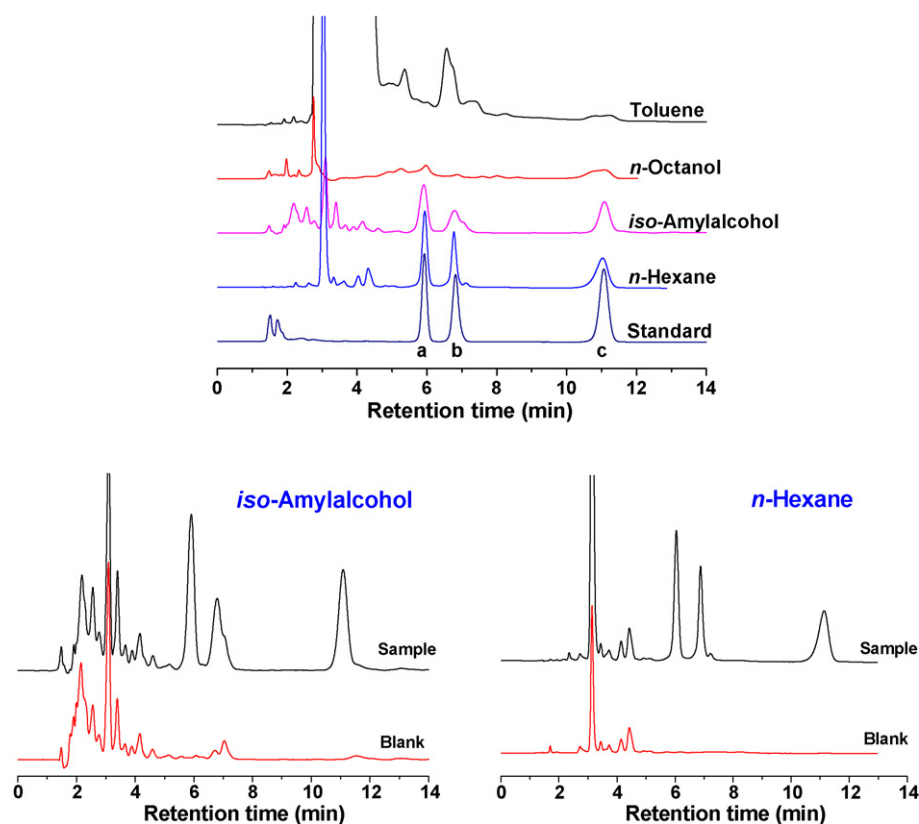[a] 1-Butyl-3-methylimidazolium hexafluorophosphats.

Fig. 9. Effect of sublation solvent on determination of pyrethroid pesticide residues by solvent sublation followed by HPLC. (a) Fenpropathrin; (b) deltamethrin; (c) bifenthrin.

Table 4
Applications of solvent subaltion in AAS analysis of metal ions.

Metal ion	Ligand	Collector	Organic solvent	Preconcentration factor (V_w[a])	Treatment time (min)	RSD (%)	Recovery (%)	Ref.
Co(II), Cu(II), Ni(II)	HQ[b]	CTAB	MIBK[c]	40 (1.0 l)	40	1.02–2.06	84–120	[70]
Au(III), Pt(IV), Pd(II)	MBT[d]	CTAB	MIBK	50 (1.0 l)	35	0.57–2.65	95.3–113.0	[71]
Zn(II), Pb(II)	Naphthoate	TBA[e]	MIBK	50 (1.0 l)	5	<10	80–100	[72]
Bi(III), In(III), Tl(III)	2-Naphthoate	TBA	MIBK	50 (1.0 l)	5	0.04–6.67	80–120	[73]
Cu(II), Mn(II), Ni(II), Zn(II)	Thiocyanate and 1,10-phenanthroline (phen)	–[f]	MIBK	200 (20.0 l)	90	<10	80–120	[74]
Zn(II), Cd(II), Cu(II)	Dithizone	NP[g]	MIBK	35 (350 ml)	30	10.5–4.26	92.7–107.3	[75]
Ni(II), Co(II), Cu(II)	Salphen	–	m-Xylene	50 (1.0 l)	20	–	97–115	[76]
Fe(II), Fe(III)	FZ[h]	TBA–HOL[i]	MIBK	200 (0.4, 0.6, 1.0 l)	10	1.3–4.3	96–104	[77]

[a] The volume of aqueous phase.
[b] The 8-hydroxyquinoline.
[c] Methylisobutyl ketone.
[d] 2-Mercaptobenzothiazole.
[e] Tetra-n-butylammonium.
[f] "–" The information is not given (or not used) in the related report.
[g] Nonylphenol polyoxyethylene ether.
[h] 3-(2-Pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine.
[i] Oleic acid.

continuous mode, a removal efficiency of $55 \pm 5\%$ was achieved for separating naphthalene from aqueous phase.

Solvent sublation is very suitable to remove the trace (or ultra trace) elements from aqueous phase to organic phase. However, in a high concentrated solution system, the separation efficiency of solvent sublation is not satisfactory. Therefore, we do not suggest solvent sublation for the real wastewater treatment, because of the secondary pollution of the organic solvent and the lower separation efficiency for the concentrated solution system.

4. Conclusion

Solvent sublation, in comparison with ion flotation and liquid–liquid extraction, has many advantages in that it allows analysis or treatment of the organic phase directly, it is not necessary to destroy the foam or emulsion, and it has high separation efficiency, high concentration coefficient, low dosage of organic solvent, soft separation process and the simple operation.

In spite of the advantages mentioned above, solvent sublation still needs so far further improvements in the theory and applications.

In the theory, the original theory is not very complete, and the present mathematical models only involve the kinetics process, not including the thermodynamic equilibrium. Therefore, to build a complete mathematical model is an arduous task. Moreover, to investigate the separation mechanisms of the new separation modes (e.g. ATPF and FCE) is also a challenging work.

In the application, some new applications should be further expanded. For example, the recovery of valuable trace metals is a very important aspect in the future, maybe they can be recovered from the sea by solvent sublation techniques. Although many works have been done about solvent sublation, but many aim at the laboratory studies, the road is very long to utilize the technique to the wastewater treatment and the usable materials recovery on the large-scale.

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