Ultrasonic assisted extraction as a potential green approach for trace metal determination in complex matrices

Sugunya Phongsirirux and Saksit Chanthai*

Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

An ultrasonic assisted extraction as a green way approach is described for simple, efficient and rapid determination of trace metals in some complex matrices by atomic absorption spectrometry and/or other techniques. Their optimized conditions are certainly investigated in details, in particular several variables that could affect the performance of the method in comparison with those of standard methods. In this review, arsenic species are focused to determine in chilli as the plant matrix, for example. This will lead to improve mild extraction method as a routine work for heavy metals in such food analysis with its emerging applications and future trends.

Key words: ultrasonic extraction, atomic absorption spectrometry, green chemistry, chilli, arsenic.
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INTRODUCTION

Fruits and vegetables, which are commonly the so-called complex matrices, are immensely valuable not only for their nutritional value but also for their efficient health functionality against various degenerative diseases caused by free radicals. They are also good source of natural antioxidants containing many bioactive components which play a significant role in prevention of free radical formation by scavenging or promotion of their decomposition. In particular, chilli pepper (*Capsicum annuum L.*) is known the most cultivated species from an economic and nutritional viewpoint worldwide [1]. Chillies are one of the widely consumed vegetables because of the combination of color, flavor, taste and nutritional value. Apart from rich source of vitamin C, it has vitamin A and E, small quantity of proteins, fats, carbohydrates and traces of minerals. It is valued for its pungency which is due to crystalline, acrid volatile alkaloid capsaicin, having diverse prophylactic and therapeutic uses in allopathic and ayurvedic medicine. These properties are also accorded due to the presence of phenolic compounds, carotenoids and capsaicinoids [2,3]. However, trace metal contamination could affect on human and plant [4] because some trace metals at low doses are essential for plants, but in higher doses they may cause metabolic disorders and growth inhibition for most of the plants species. The trace metals are a toxic group used to describe more than a dozen elements that are metals or metalloid [5,6] such as lead, nickel, zinc, chromium, cadmium, copper, iron and arsenic etc. Human activity affects the natural geological and biological redistribution of trace metals through pollution of air, water, animal, soil and plant [7]. The effect of trace metals on health including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead) and cancer (e.g., arsenic).

Trace heavy metals have long been known as toxic agents in human being. Especially, arsenic (As) is also a poisonous metal that is found in inorganic and organic forms in water, soil, dust, wood, plant and other material [8]. Arsenic containing pesticides, wood preservatives [9] and other agricultural products can lead to the accumulation of arsenic and other toxic metals in soil and plants and trace amounts of toxic metals, including arsenic found in food and feedstuffs [10-12]. The determination of toxic nonessential element arsenic species in chilli pepper is an important screening procedure in the studies of toxicity and elemental chemical and biological effects of chilli pepper. The arsenic compounds in plant tissues reflected predominantly the extractable portions of arsenic

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compounds present in soil after amendment, and this pattern was more significant in the first part of vegetation period. The results confirmed the ability of generative parts of plants to accumulate preferably organic arsenic compounds, whereas in the roots and above ground biomass, mainly inorganic arsenic species are present. Evidently, the source of soil arsenic contamination affects significantly the extractable portions of arsenic compounds in soil and subsequently the distribution of arsenic compounds within the plants [13,14].

Arsenic is widely distributed in large number of minerals. Arsenic concentrations in soils and sediments are dependent on the geological conditions as well as on anthropogenic activities, e.g., the use of pesticides, mining activities, or industrial processes. Humans are exposed to many different forms of inorganic and organic arsenic species, arsenicals, in food, water and other environmental media. Arsenic in foods occurs due to environmental contamination. Foods of animal or vegetable origin have a relatively low concentration. Furthermore, arsenic must be extracted from solid samples and presents in an aqueous form for speciation analysis by the more common methods such as ultrasonic system. It has been routinely applied in laboratories as an alternative sample preparation procedure for challenging matrices that are usually recommended for atomic spectrometry. The physical effect produced by ultrasonic system (either bath or probe) includes cavitation, which consist of the nucleation, growth, and collapse of short-lived bubbles, which are formed in liquids/solutions that are exposed to low-frequency ultrasonic waves (<1 MHz). During sample preparation, cavitations favor the extraction of chemical species from solid materials through dissolution or complete mineralization performed at ambient temperature into dilute acid solutions. Therefore, the use of ultrasonic-assisted extraction into dilute acid solutions for the determination of macro- and micronutrients in agro-industrial samples avoids the use of concentrated acid solutions for sample digestion [15].

This review is to pave the way for simple and accurate method that suitable for routine application to determine of some metals available in such plant samples by flame atomic absorption spectrometry (FAAS) and some metal speciation (inorganic and organic compounds) analysis using flow injection-hydride generation atomic absorption spectrometry (FI-HGAAS). This will lead the development of a simple and robust sample preparation procedure that uses an ultrasonic-assisted extraction system for the determination of total metals using FAAS to surplus conventional sample pretreatment procedures based on acid digestion.

MATERIALS AND METHODS

2.1 Determination of arsenic in real samples
In many cases, arsenic has been chosen which is known to be toxic since ancient time, for example. This toxicity can make the high levels of arsenic found in plants growing on many contaminated sites problematic for plant consumers [16,17]. Many arsenic compounds present in the terrestrial and marine environments have been detected [18,19]. As(III), As(IV), methylarsonic acid (MA) and dimethylarsinic acid (DMA) are the predominant arsenic species found in terrestrial biota, including plants. Chronic exposure to arsenic, particularly inorganic arsenite (As(III)) and arsenate (Ar(V)), has been implicated in many physiological disorders and various types of cancers. Since the toxicity of arsenic depends on its chemical form, both speciation and quantitative determination of arsenic are essential.

The determination of arsenic in samples can be done by various techniques including atomic absorption spectrometry (AAS) [20], inductively coupled plasma-mass spectrometry (ICP-MS) [21,22], electrothermal atomization atomic absorption spectroscopy (ETAAS) [23,24], hydride generation coupled with atomic absorption spectroscopy (HGAAS) [25], or coupled with atomic fluorescence spectroscopy (HGAFS) [26], high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) [27], graphite furnace atomic absorption spectrometry (GFAAS) [28,29], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [30], high performance liquid chromatography-hydride generation-inductively coupled plasma-mass spectrometry (HPLC-HG-ICP-MS) [31], ultraviolet-visible spectrophotometer [8] and electrochemistry [32]. The analytical techniques are suitable for determination of arsenic due to high precision, sensitivity and low detection limit. However, it is notable that HGAAS technique is widely used for determination of arsenic when compared with those mentioned techniques. HGAAS has been frequently used for direct determination of arsenic because of use, quick operation, high sensitivity, low cost and low detection limit. Literatures on determination of arsenic by FI-HGAAS and other published methods are summarized in Table 1 and 2.

However, HGAAS cannot be a direct determination of organic arsenic. Although the analytical methods for determination of organic arsenic compounds have been conducted, their limited and complex instrumentation are encountered. So, this study focuses on the developed method for organic arsenic analysis using ultrasonic assisted extraction (UAE). UAE is an easy, convenient, and fast way of desorbing inorganic and organic pollutants from sediments, soils and biological samples [33]. The procedure for arsenic extraction in mining residues employing

UAE and determination by HG-ICP-OES was developed [34]. The analytical method provided analytical precision and a better evaluation of environment impact of mining residue deposits. Optimal conditions for UAE were obtained by an evaluation of parameters such as the position of the sample flask inside the ultrasound bath and temperature as a function of the immersion time. The results for the extraction of arsenic in the mining waste by employing a CCD design for the use of an ultrasonic bath for energy proved to be quite satisfactory. The arsenic concentration obtained using the UAE was superior to that obtained by the standard method performed by microwave assisted extraction (MAE).

Table (1): Literature reviews on the determination of arsenic by FI-HGAAS

Sample	Recovery (%)	LOD	Ref.
Thai fruit wine and distilled spirit	91.4-119.0	As(III) 0.49,1.9 ppb As(V) 0.35,0.63 ppb total As 0.47 ppb	9
acid digest of plant and peat	-	23 ppb	35
phosphate-fertilizer and phosphate-rock	100.0-108.0	0.1 ppb	36
some contaminated ground water	-	0.4 ppb	37
environmental solid	-	As(III) 0.07 ppb total As 0.06 ppb	38
water, urine and plant	99.0-107.0	As(III) 0.1 ppb	39
environmental sample	102.0-114.0	0.5-1.8 ppb	40
cigarette tobacco	93.0-94.0	2.6 ppb	41

Table (2): Literature reviews on the determination of arsenic species by other published methods

Sample	Method	Recovery (%)	LOD	Ref.
rice flour	HPLC-ICP-MS	94.7-102.1	As(III) 0.01 ppb As(V) 0.01 ppb DMAA 0.03 ppb	42
marine sediment	HPLC-ICP-MS	As(III) 89 As(V) 104	-	43
blubber of ringed seal	HPLC-ICP-MS	-	-	44
alga samples	HPLC-HG-ICP-AES	93 and 115	0.5 ng As(III), 2.0 ng DMA, 1.0 ng MMA, 2.0 ng As(V)	31
Red tangerine peel	HGAFS	94.9-97.7	0.039 ppm	45

2.2 Sample preparation by ultrasonic method
The extraction methods of plant commonly include hot water extraction (HWE), microwave assisted extraction (MAE), pressurized liquid extraction (PLE), ultrasonic solvent extraction (USE) and ultrasound-assisted extraction (UAE). Although the main advantage of applying microwave is that it is time saving but its disadvantage in homogeneous heating [46,47]. Thus, the use of an ultrasound is more convenient and affordable. Ultrasound processing presents a certain number of parameters that should be carefully studies in that they can influence the process. Ultrasonic frequency is one of important operating parameters and has a strong effect on extraction yield. In general, for ultrasonic cavitation, not all bubbles are capable of producing significant cavitation effects. The greatest coupling of the ultrasonic energy will occur when the natural resonance frequency of the bubble is equal to the ultrasonic frequency. The resonance frequency of the bubble is equal to the ultrasonic frequency. The resonance frequency equation of extraction bubble was deduced by Huang et al. [48]. It suggested that under the conditions described to study ultrasonic extraction, the yield in liquid medium can reach a maximum value at the optimum ultrasonic frequency which helps to promote bubbles division by driving the bubbles into resonance. Therefore, determination of optimum ultrasonic frequency is a very important research subject, which may improve extraction yields for natural products.

Table (3): Literature reviews on the sample preparation by ultrasound-assisted extraction (UAE)

Sample	Analyte	Reagent	Power	Ref.
oilseed crops	copper, manganese, calcium and magnesium	10 mL of 1.40 M HNO_3	40 kHz	15
flower buds of sophora japonica	rutin	water and methanol	20 kHz 27 W	50
tobacco (*Nicotiano tabacum* L.) seeds	oil	*n*-hexane and petroleum ether	40 kHz	51
caraway seeds	carvone and limonene	*n*-hexane	20 kHz 150 W	52
black tea	polyphenols	water	25 kHz 150 W	53

Ultrasound-assisted extraction is a novel method to effectively extract the targeted components from plant products which has been proven to significantly increased extraction yield together with shorter time, lower temperature and

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smaller solvent. Recently, many studies have reported that higher extraction yields could be achieved when an UAE method was adopted on many plant products, such as rutin from flower buds of Sophora japonica, oil from tobacco (*Nicotiana tabacum* L.) seed, carvone and limonene from caraway seeds, polyphenols from black tea, extraction of carotenoids, pectins from grape pomace, D-pinitol from carob pods and vanillin from vanilla pods. Those studies mainly looked at optimization of other extraction conditions with regards to efficiency and/or yield [49]. Literature reviews on the sample preparation by the ultrasonic assisted extraction are summarized in Table 3.

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