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Microextraction based on solidified floating organic drop coupled with ETAAS for the determination of lead in herbs

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Abstract

A rapid, inexpensive and practical solidified of floating organic droplet microextraction (SFODME) prior to electrothermal atomic absorption spectrometry (ETAAS) was proposed for lead (Pb) determination in herb samples. For SFODME procedure, 1-(2-pysidylazo)-2-naphthol was used as a complexing agent. Analytical parameters influencing the extraction efficiency, *i.e.* types and volume of extracting solvent, concentration of 1-(2-pyridylazo)-2-naphthol, pH, extraction temperature and time were optimized. Under the optimized conditions, LOD and LOQ were 0.064 and 0.214 µg L^{-1}, respectively, and an enrichment factor was achieved at 18.71 with the relative standard deviation ranging from 1.3 to 2.5% (n=6). The proposed method was effectively applied to the determination of lead in Spinach leaves (SRM-1570a) and Thai herb samples with acceptable results.

Introduction

In recent years, consumption of herbs for health benefits are not only common in Asia but are also widely used around the world. They can also have used for phytotherapy, which is using plants for relieve and treat of diseases. Medicinal plants have been increasingly used due to their mild and low side effects (Rates 2001; Oviedo *et al.* 2013). Manufacturers are only required to carry out the analysis of contaminants such as hazardous metals in the raw plant materials. However, the extracts normally do not define the quality and amount of contaminate present. In order to help the quality estimation of these products, the analysis of contaminates can reduce health risk, especially by toxic metals. Therefore, it is necessary to monitor the amount of toxic heavy metals in these samples (Khan *et al.* 2008). Lead (Pb) results in harmful effects to the renal, endocrine, digestive, cardiovascular, reproductive systems as well as affecting the development of neurologic system (Solidum 2014). The World Health Organization (WHO) has suggested 10 mg kg^{-1} as the maximum acceptable concentration of Pb in therapeutic plants. Literature review found that Pb was mostly found in a variety of herbs and showed Pb contents between 0.2 to 2.7 mg kg^{-1} (Divrikli *et al.* 2014). Consequently, traceable and reliable measurement of Pb is essential for the safety and risk assessment for the wide use of traditional and medicinal herbs. Currently, there are some variety methods related to modern instrumentation that have been widely used for heavy metal determination; these include ICP (MS and AES) (Zhao *et al.* 2012; Sorbo *et al.* 2014; Deng *et al.* 2015; Tai *et al.* 2016) and AAS (Demirtaş *et al.* 2015; Batista *et al.* 2016;

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Zhong *et al.* 2016). However, trace determination of Pb in herb samples is relatively inconvenient because of the matrix effect and low concentration of Pb. To answer this problem, separation or pre-concentration techniques are required. Numerous techniques have been examined for pre-concentration/determination of trace Pb, namely liquid phase extraction (Ikeda *et al.* 1998; Dapaah *et al.* 1999; Zendelovska *et al.* 2001) and solid phase extraction (Dadfarnia *et al.* 2007; Ghaedi *et al.* 2007; Tharakeswar *et al.* 2012). Although, conventional extraction methods can be obtaining reliable results, they usually have some disadvantages such as required long time, labor intensive and/or required large volumes of extracting solvent. In order to find a solution to pre-concentration, microextraction techniques, namely single drop microextraction (SDME) (Maltes *et al.* 2008; Manzoori *et al.* 2009), solid phase microextraction (SPME) (Zhang *et al.* 1994; Górecki and Pawliszyn 1996; Djozan and Assadi 2004) dispersive liquid liquid microextraction (DLLME) (López-García *et al.* 2014; Jalbani and Soylak 2015; Rosa *et al.* 2015) and hollow fiber liquid phase microextraction (HFLPME) (Xia *et al.* 2007; Jiang *et al.* 2009; Saleh *et al.* 2009) have been reported. Solidified of floating organic droplet microextraction (SFODME) was developed in 2007 (Lam *et al.* 2010). This microextraction methodis different from other liquid phase micro-extraction that uses a microliter volume of the extractant)melting point around 10 – 30 °C(delivered to the sample solution, stirred for an appropriate time, and then relocated into an ice bath. After the extracting solvent becomes solid,it is transferred into another vial and melted immediately. Finally, the solution is directly determined the analyte concentration.

From the literature, there are only few reports related to separation/pre-concentration of Pb in herb samples (Solidum 2014; Tai *et al.* 2016, Lam *et al.* 2010; Yavuz *et al.* 2016). Therefore, SFODME technique combination with ETAAS for the Pb determination in herb samples was conducted in this work. We selected 1-(2-pyridylazo)-2-naphthol as the complexing agent and the several parameters influencing the extraction efficiency were optimized.

Experimental

Standard solution of Pb 1,000 mg L^{-1} was obtained from AVS Titrinorm (VWR International, Belgium) and working standard solutions were freshly prepared with deionized water. Chelating reagent was prepared by dissolving an appropriate amount of 1-(2-pyridylazo)-2-naphthol (Acros organics, US) in ethanol. 1-undecanol was purchased from Merck (OHG, Germany). Buffer solutions of ammonium acetate (pH 4, 0.2 mol L^{-1}), phosphate (pH 7, 0.2 mol L^{-1}), and ammonium chloride (pH 9, 0.2 mol L^{-1}) were used to adjust the pH in the range of 3.0 – 12.0. The laboratory glassware were soaked in nitric acid (10%) for 24 h and rinsed with deionized water before use. The certified reference material was used for method validation: Spinach leaves (SRM-1570a) was purchased from National Institution of Standard and Technology.

The experiments were performed with an electrothermal atomic absorption spectrometer (Varian Model SpectrAA 220Z) and the instrument parameters were demonstrated in Table 1. The pH of solution were measured by pH meter (Metrohm, 827 pH lab) combined glass electrode.

For SFODME extraction procedure, blank solution, 15.00 µg L^{-1} of standard (Pb) or sample solution (13.0 mL) was adjusted to pH 6 with phosphate buffer and 0.5 mL of 1-(2-pyridylazo)-2-naphthol (3.0 mmol L^{-1}) were mixed in a screw-cap glass vial (15 mL). Then, 90 µL of 1-undecanol was added to the aqueous solution and the solution was stirred for 40 min at 750 rpm at room temperature. After this procedure, the glass vial was transferred into an ice bath for 5 min and the organic phase eventually turned to solid. This solvent was simply relocated into the ETAAS vial by a small spatula and the droplet was melted immediately. Finally, the organic drop was diluted to 500 µL with ethanol and determined by ETAAS.

Thai herb samples were collected from Phitsanulok (Thailand) and dehydrated with oven (70°C) for one hour. After that, samples were sieved through a 100 µm sieve (Oviedo *et al.* 2013). 4 mL of concentrated HNO_3 and H_2O_2 at a ratio 3:1 was added and thoroughly mixed with 0.01 g of the sieved sample. The solution was heated on the hotplate at 120 °C until the red brown smoke disappeared. The residue was filtrated and diluted to 25 mL with volumetric flask. This solution was then used for extraction by SFODME technique. The proposed method was validated with recovery study from spiked known amount of Pb standard solution at the concentration of 5.00 and 10.00 µg L^{-1} to herb samples before digestion.

Table 1. Instrumental parameters and furnace heating program for determination of Pb.

Instrumental parameter	Value	
Lamp current (mA)	10	
Wavelength (nm)	283.3	
Spectral resolution (nm)	0.5	
Background correction	Zeeman background correction	
Injected sample volume (µL)	10	
Chemical modifier	$Pd(NO_3)_2$ 1000 mg L^{-1} 5 µL	
Furnace program		
Stage	Temperature (°C)	Time (s)
Drying	95	15.0
Ashing	400	19.0
Atomization*	2 100	2.9
Cleaning	2 100	2.0

*Reading step

Results and Discussion

1-(2-pyridylazo)-2-naphthol is a ligand that can interact with many metal ions to form complexes, such as, Cd(II) or Pb(II) (Tharakeswar *et al.* 2012), as shown in Fig. 1. 1-(2-pyridylazo)-2-naphthol is relatively soluble in aqueous condition but its complexes have low polarity. Also, in the preliminary experiment, the Pb-1-(2-pyridylazo)-2-naphthol complexes are well soluble in 1-undecanol and this ligand can be used for the separation and extraction of Pb by SFODME method followed by ETAAS detection. In order to get high extraction efficiency, the effect of different parameters was considered and optimized.

Selection of extracting solvent

In the SFODME technique, the suitable organic solvent has a remarkable effect on the formation of metal-ion complexes. Furthermore, it must have a melting point around 10 to 30°C (near room temperature), low toxicity, and high enrichment factor (Yavuz *et al.* 2016). In this experiment, two extracting solvents, 1-dodecanol and 1-undecanol, were compared and 1-undecanol was chosen as it gave the highest relative absorbance. Since the volume of organic solvent could affect the pre-concentration factor (Li *et al.* 2006), therefore, different volumes (20 – 150 µL) of 1-undecanol were investigated in the extraction procedure. When increasing the volume of 1-undecanol, the relative absorbance increased until 90 µL and then relative absorbance decreased. This could be owing to the transportation of analyte, which is associated with increasing the surface contact between the layers of two liquids. From the results, 90 µL of 1-undecanol was considered as optimized extraction volume.

pH value

Generally, the extraction efficiency depends on pH value of the aqueous solution and have a significant effect to the complex formation of Pb-1-(2-pyridylazo)-2-naphthol and subsequently the SFODME extraction. In this experiment, pH of solution was controlled in the range of 3.0 – 12.0

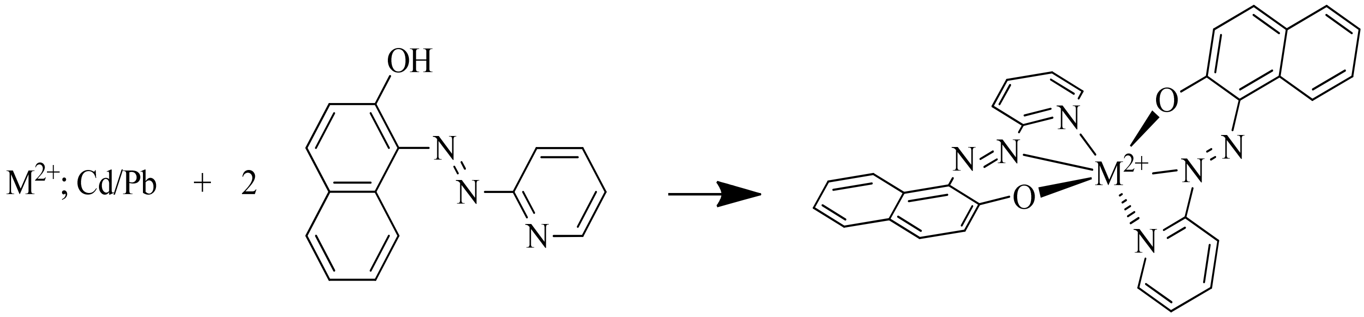

Fig. 1. Chemical structure of metal-PAN complex.

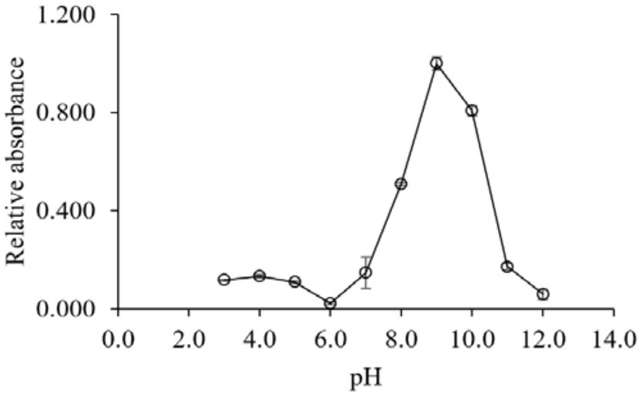

Fig. 2. Effect of the pH. Extraction conditions: Sample volume – 13 mL; extraction solvent – 1-undecanol; PAN concentration – 3.0 mmol L^{-1} – 0.5 mL; extraction time – 30 min; stirring rate – 625 rpm at room temperature.

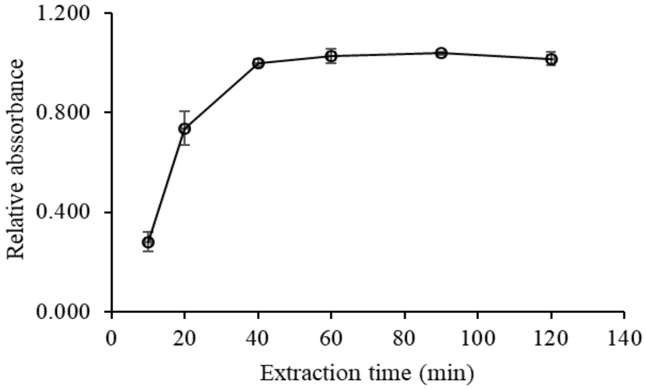

Fig. 3. Effect of the extraction time. Conditions are the same as in Fig. 2. except extraction time, at pH 9 and concentration of PAN, 3.0 mmol L^{-1}.

using different buffer solutions. The result is illustrated in Fig. 2 and it is clearly seen that the best relative absorbance was obtained at pH 9. At this pH, Pb-1-(2-pyridylazo)-2-naphthol complexes were effectively extracted into the organic solvent. Therefore, pH 9 was chosen for further experiments.

1-(2-pyridylazo)-2-naphthol concentration

Due to the amount of 1-(2-pyridylazo)-2-naphthol can affect to the extraction efficiency, the concentration of 1-(2-pyridylazo)-2-naphthol was consequently investigated. The result showed that the relative absorbance was increased when increasing the concentration of 1-(2-pyridylazo)-2-naphthol up to 3.0 mmol L^{-1} and this continued constant even as the amount of 1-(2-pyridylazo)-2-naphthol is increased further. Therefore, 3.0 mmol L^{-1} of 1-(2-pyridylazo)-2-naphthol was selected for further studies.

Extraction time

In order to obtain high sensitivity, good precision and speed up the extraction process, it is required to investigate the effect of the extraction time to ensure the completion of extraction between organic phase and sample solution. The extraction time was studied between of 10 – 120 minutes. The result revealed that the relative absorbance was increased and steadied after 40 minutes (Fig. 3). Therefore, 40 minutes of extraction time was selected for subsequent experimentations.

Stirring rate

To reduce the time required to reach the equilibrium between the extracting solvent and aqueous solution (Li *et al.* 2006), the effect of stirring rate was studied between of 250 – 1250 rpm. For the optimized experimental conditions, 750 rpm was selected.

Extraction temperature

At higher temperatures, the extraction kinetics influence the mass transfer of the analyte between the aqueous solution and the extracting solvent (Ghanbarian *et al.* 2013). Extraction temperature was studied over a temperature range of 20 – 80°C. From the results, the relative absorbance increased until 50°C, after that relative absorbance decreased when increasing extraction temperature. This phenomenon may be due to the solubility of organic solvent increased and the breakdown of organic solvent at high temperature (Bidabadi *et al.* 2009). Therefore, the extraction temperature was controlled at 35°C.

Table 2. Effect of interfering ions on the quantitative recovery of 10 μg L^{-1} Pb.

Ions	**Mole ratio (Ion/analyte)**
Na^+, K^+, Cr^{3+}, NO_3^-, SO_4^{2-}, PO_4^{3-}	10 000
Cd^{2+}, Mg^{2+}, Fe^{3+}, As^{3+}	100

Table 3. Application of presented method in certified reference material and Thai herb.

Samples	Certified (μg g^{-1})	Added (μg L^{-1})	Concentration in digested solution (μg L^{-1} ± SD)	Concentration in sample (μg g^{-1} ± SD)	Recovery (% ± SD)
SRM-1570a (Spinach leaves)	0.2	–	–	0.20 ± 0.01	100.0 ± 1.1
Zingiber officinale		–	3.91 ± 0.55	0.48 ± 0.07	–
		5.00	9.43 ± 0.67	–	110.5 ± 1.7
		10.00	14.19 ± 0.41	–	102.9 ± 3.3
Coscinium fenestratum		–	0.76 ± 0.02	0.09 ± 0.01	–
		5.00	5.74 ± 0.19	–	99.5 ± 4.2
		10.00	10.80 ± 0.39	–	100.3 ± 3.9
Curcuma longa		–	1.72 ± 0.34	0.20 ± 0.04	–
		5.00	6.62 ± 0.28	–	98.1 ± 1.3
		10.00	11.96 ± 0.47	–	102.4 ± 3.7
Piper retrofractum		–	2.64 ± 0.68	0.31 ± 0.09	–
		5.00	7.79 ± 0.97	–	103.1 ± 4.6
		10.00	13.01 ± 0.89	–	103.7 ± 9.1
Tinospora crispa		–	1.54 ± 0.26	0.18 ± 0.03	–
		5.00	6.77 ± 0.18	–	104.7 ± 1.0
		10.00	12.00 ± 0.34	–	104.6 ± 3.1
Cryptolepis buchanani		–	2.32 ± 0.26	0.27 ± 0.03	–
		5.00	7.43 ± 0.25	–	102.3 ± 0.8
		10.00	12.78 ± 0.30	–	104.6 ± 1.4
Butea superba		–	1.42 ± 0.20	0.16 ± 0.02	–
		5.00	6.44 ± 0.23	–	100.4 ± 0.7
		10.00	11.48 ± 0.19	–	100.6 ± 1.0
Moringa oleifera		–	2.14 ± 0.38	0.25 ± 0.05	–
		5.00	7.26 ± 0.34	–	102.4 ± 1.9
		10.00	12.33 ± 0.78	–	101.9 ± 5.0
Kaempferia parviflora		–	1.65 ± 0.02	0.19 ± 0.01	–
		5.00	6.80 ± 0.23	–	103.1 ± 1.9
		10.00	11.79 ± 0.21	–	101.4 ± 4.3

Addition of salt

The addition of salt in aqueous solution can change the physical properties of the Nernst diffusion film and reduce the rate of diffusion of the interest analytes into the drop (Sobhi *et al.* 2009). Also, the effect of salt addition on SFODME technique was studied by adding different quantities of NaCl and KCl at 0–5% (w/v). The results exhibited that when increasing amount of salt, the relative absorbance decreased. Consequently, the extraction procedures were accomplished without salt addition.

Interfering ions

In the SFODME procedure (Wang *et al.* 2011; Chen *et al.* 2013; Dadfarnia *et al.* 2013), many other heavy metal ions can form complexes with the chelating reagent and can co-extraction with interested metal. To investigate the selectivity of the proposed procedure, the effect of interfering ions on Pb determination in herb samples by SFODME was investigated considering from the percentage recovery. These coexisting ions were considered to interfere in Pb determination if the percentage recovery was over ±5%. The results were demonstrated in Table 2.

Analytical performance

Under the optimized condition for SFODME, the analytical performance for Pb determination was evaluated. The linear range of Pb concentration was 0.5 – 30.0 μg L^{-1} (Y = 0.0131X + 0.0100, where Y is the concentration of analyte) with r^2 = 0.9996. The LOD and LOQ were 0.064 and 0.214 μg L^{-1}, respectively and %RSDs varied from 1.27% to 2.48% (n=6). The enrichment

Table 4. Comparison of analytical performance of the proposed method with other methods for determination of Pb.

Method	Sample	LOD ($\mu g\ L^{-1}$)	Linear range ($\mu g\ L^{-1}$)	RSD (%)	Reference
CPE-GFAAS	Water	0.08	up to 30.0	2.8	Chen *et al.*, 2005
SDME-ETAAS	Water	0.2	1.0 – 15.0	4	Maltes *et al.*, 2008
DLLME-ETAAS	Water	0.02	0.05 – 1.00	2.5	Naseri *et al.*, 2008
SPE-ETAAS	Seawater	0.12	0.1 – 10.0	3.2	Alonso *et al.*, 2006
SFODME-ETAAS	Water and infant formula	0.058	0.2 – 10.0	8.8	Chamsaz *et al.*, 2013
SFODME-ETAAS	Herbs	0.064	0.5 – 30.0	2.48	This work

factor, EF (Dadfarnia *et al.* 2007; Durukan *et al.* 2011) defined by the division of the slope of calibration equation after pre-concentration and that of previous pre-concentration by ETAAS was accomplished at 18.71 for 13 mL of sample solution.

To guarantee the accuracy of the method, the determination of certified reference material SRM-1570a (Spinach leaves) was used for method validation through recovery experiments. The results are presented in Table 3 and it was indicated that a found concentration agreed well with certified value. Satisfactory recoveries revealed that SFODME-ETAAS method was effective for the pre-concentration/determination of lead. A comparison of analytical performance of the proposed method with others is shown in Table 4 and indicates its higher effectiveness to Pb determination at lower detection limit and better precision than previously reported methods.

Determination of Pb in Thai herb samples

The procedure was applied to the determination of Pb in Thai herb samples. The samples were prepared as described and 13 mL of it was treated according to the same procedure. The proposed method was validated with recovery study from spiked known amounts of Pb standard solutions. Recoveries from spiked standard solution to the samples are shown in Table 3. It was found that recoveries were in the range of 98 – 110.5% which confirms the validity and accuracy with acceptable results.

Conclusions

SFODME-ETAAS method was assessed for the pre-concentration and determination at trace $\mu g\ L^{-1}$ level of Pb in Thai herb samples. This method provided several advantages such as simple to operate, minimum consumption of extraction solvent and the solidified organic phase is simply collected and separated from the aqueous sample. Additionally, on-going research related to the application of SFODME method for pre-concentration/determination of other heavy metals in different types of sample matrices using new chelating reagents are subjects on ongoing research.

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