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Solid-Phase Extraction with Diethyldithiocarbamate as Chelating Agent for Preconcentration and Trace Determination of Copper, Iron and Lead in Fruit Wine and Distilled Spirit by Flame Atomic Absorption Spectrometry

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Abstract: Some heavy metals that present in wine and distilled spirit as background contamination are generally found at trace level particularly less than detection limit of common analytical techniques including flame atomic absorption spectrometry (FAAS). Thus, preconcentration method of the trace metals was developed. The optimum conditions for diethyldithiocarbamate (DDTC) complexes of Cu, Fe and Pb were then investigated for the preconcentration step using C_{18} solid-phase extraction prior to measurement by FAAS. The preconcentration factor of 15-fold was obtained with the appropriate ratio of sample volume used (150 mL) to 10 mL final volume giving their method recoveries of Cu, Fe and Pb found in the ranges of 96.5-107, 102-116 and 91.7-107%, respectively. Precision determinations (n = 10) for 0.1 mg L^{-1} of Cu, Fe and Pb each in a model solution were 3.7, 4.2 and 7.1 %RSD respectively. The detection limits (3SD) of Cu, Fe and Pb were found to be 1.4, 3.3 and 5.7 μg L^{-1}, respectively. The developed method was applied to ten samples of local fruit wines and five samples of distilled spirits, resulting in the ranges of 0.012-0.80 and 0.12-8.8 mg L^{-1} for Cu; 0.18-3.4 and 0.036-0.29 mg L^{-1} for Fe and 0.0070-0.053 and 0.014-0.026 mg L^{-1} for Pb, respectively. Therefore, the method is simple and inexpensive for routine analysis of the trace metals in these samples to overcome limit of detection of the instrument used.

Keywords: Fruit wine, Distilled spirit, Diethyldithiocarbamate, Solid-phase extraction, FAAS, Preconcentration

Introduction

Fruit wines can be widely produced and consumed as alcoholic beverage throughout Thailand. Wine that made from fruits, such as mangosteen, longan, *etc*. must be identified by the fruits used, for instance, mangosteen wine, longan wine and so on. Distilled spirit is also an alcoholic one usually produced from rice wine or so-called "Satho". Daily consumption of wine and distilled spirit in moderate quantities may contribute significantly to the requirements of human organism for essential elements such as Cu and Fe. But some metals such as Pb and As are known to be potentially toxic[1-5]. Analysis of certain elements in wine and distilled spirit is thus of interest due to their toxicity in case of excessive intake.

Most countries have specific legislation concerning the maximum permissible content of some metals, especially Cu, Fe, Pb and As, in wine and distilled spirit[6-9]. Thai industrial standards institute (TISI) has been responsible for quality control of these local products in terms of limiting concentrations of the heavy metals normally found in wine and distilled spirit. The method proposed by the association of official analytical chemistry (AOAC) and/or other methods for the determination of Cu, Fe, Pb and As in wine and distilled spirit have been used[10-18]. Generally, determination of metals in beverage samples can be done by various instrumental techniques[19-31]. Flame atomic absorption spectrometry (FAAS) is the most commonly used technique for the metals determination. However, there are some difficulties to determine a trace level of heavy metals in beverage samples. First, it is a very low concentration of heavy metals, which may be lower than detection limit of many techniques including FAAS. The second one is the interfering effect of some matrices present in the samples. Direct FAAS determination of heavy metals in wine has been reported strong matrix interference especially in the case of red wines. Therefore, preliminary sample digestion is still recommended. Moreover, direct aspiration of wine and distilled spirit can cause flame fluctuations and accumulation of solid deposits on the burner head. Sometimes, the acids used for sample digestion may cause inaccuracies in method, which is based on external calibration with dilute aqueous standard solution. Thus, preconcentration method is still needed to improve the detection limit and some extent of selectivity for the determination by FAAS[31-37]. Solid-phase extraction (SPE) has been widely used for the preconcentration/ separation of trace metals and clean up or removal of matrix interference in aqueous samples[38-43]. As chelating agent, sodium diethyldithiocarbamate (DDTC) has a strong tendency to form stable heavy metal complexes. At the same time, it does not react with alkali, alkaline earth elements and some other metals. SPE method can be preconcentrated and separated the metal-DDTC from a large excess of other matrix interferences in several samples by using a C_{18} column which exhibits a very strong retention to non-polar derivatives of the target metals[44-47].

For the quality control of trace amounts of Fe, Cu, Pb and As in local thai fruit wine and distilled spirit samples under TISI legislation. Since ultratrace analysis of As in these samples can be done without preconcentration by HG-AAS[48]. The aim of the present study is to investigate simple and accurate method that is suitable for routine application for Cu, Fe and Pb determinations in these samples by FAAS using DDTC as chelating agent associated with C_{18} solid-phase extraction for the preconcentration.

Experimental

All of reagents used were analytical reagent grade. The AAS standard solutions (1,000 mg L^{-1}) of Cu, Fe and Pb were obtained from Carlo Erba (Italy). Hydrochloric acid, absolute ethanol,

sodium acetate, sodium citrate dihydrate, sodium diethyldithiocarbamate and sodium hydroxide were also from Carlo Erba (Italy). Nitric acid 65% (w/v) was obtained from Merck (Germany). Di-sodium hydrogen phosphate anhydrous was obtained from Fluka (Switzerland). Hydrogen peroxide was of Ajex Chemical (Australia). Acetic acid was of Analar (England). All aqueous solutions were prepared with de-ionized water (Milli Q Millipore 18.2 MΩ cm^{-1} resistivity) by simplicity water purification system, model simplicity 185, Millipore Corporation (USA).

Instruments and apparatus

An atomic absorption spectrometer of the Perkin-Elmer instruments (USA), model A analyst 100, AA win lab software was used in association with a 10-cm long slot burner head, hallow cathode lamp and air/acetylene flame. The spectra of the metal complexes were obtained by UV-visible spectrophotometer, model Agilent 8453 (Germany) equipped with a 1 cm quartz cell. pH measurement was performed on pH meter from Denver Instrument, model 251 (USA). The C_{18} cartridge (500 mg) was obtained from Supelco (USA). All glassware were cleaned by soaking in 10% (v/v) HNO_3 overnight and rinsed three times with de-ionized water prior to use.

FAAS instrument for all determinations of Cu (324.8 nm, 0.7 nm slit width), Fe (248.3 nm, 0.2 nm slit width) and Pb (283.3 nm, 0.7 nm slit width) was operated at the optimum conditions suggested by the manufacturer's manual, except some conditions such as air flow rate (5 mL min^{-1}), acetylene flow rate (2.5 mL min^{-1}) and sample flow rate (7 mL min^{-1}) were re-optimized in this study. The AAS measurement was set as background corrected atomic absorption mode.

Wine and distilled spirit samples

Ten kinds of Thai fruit wines were purchased from local market in Khon Kaen province, Thailand. These fruit wines are locally produced by small holders through out Thailand and are available in the market. Five red wines were made from its color fruit materials including black galingale (RW01), Indian mulberry (RW02), mangosteen (RW03), maow (RW04) and bel fruit (RW05). Five white wines were also made from its fruits including longan (WW01), Indian gooseberry (WW02 and WW03), black glutinous rice (WW04) and pineapple (WW05). In case of distilled spirit samples, all of five samples were made from fermented rice as based materials including Kang Koaw (DS01), Bau Yai (DS02), Ta-Tiang (DS03), Pla-Mungkorn (DS04) and Bang Yikun (DS05). These wine samples were kept cool in refrigerator before use, while distilled spirit samples were stored in room temperature.

Preparation of standard solutions

A working solution of 50 mg L^{-1} Cu was prepared by diluting 5 mL of its stock solution (1,000 mg L^{-1}) to 100 mL with de-ionized water. For working solutions of Fe and Pb were daily prepared in the same manner. The calibration curve was established using the standard solution prepared in 3 mol L^{-1} HNO_3 by dilution from the working solutions and not introduced to the preconcentration procedure. The standard solution of Cu was contained 0.5, 1.0, 1.5, 3.0 and 5.0 mg L^{-1} and Fe was contained 0.5, 1.5, 3.0, 5.0, 10 and 15 mg L^{-1}, and Pb was contained 0.5, 1.0, 1.5, 3.0 and 5.0 mg L^{-1}, respectively. Their standard solution was determined by FAAS.

Preparation of C_{18} cartridge

The C_{18} sorbent packing material was firstly washed by passing 5 mL of 3 mol L^{-1} HNO_3 solutions twice in order to remove trace metals adsorbed on the packing material.

Then, the cartridges were rinsed with 5 mL of deionized water twice and they were activated by washing with 5 mL of ethanol twice and rinsed with 5 mL of deionized water twice. At the beginning of next analysis cycle, the cartridge was rinsed with deionized water, washed with ethanol and again rinsed with deionized water as the same manner described.

Metal-DDTC complex and preconcentration

Performance of the C_{18} cartridge was tested with model solutions prior to its application to real samples. Trace metals of Cu, Fe and Pb were complexed with DDTC under optimized conditions prior to preconcentration step by SPE method. The parameters that influence the preconcentration of these elements such as pH, eluent concentration were also optimized.

Effect of DDTC concentration

A 0.01 mol L^{-1} DDTC solution was prepared by dissolving a required amount of sodium diethyldithiocarbamate (MW 225.23 g mol^{-1}) in deionized water. The DDTC solution was prepared daily. Various concentrations of DDTC were also carried out. The DDTC concentration was investigated in the range of 1.0×10^{-4}- 2.0×10^{-2} mol L^{-1} while 3 mol L^{-1} HNO_3 was used in an elution step of the metal-DDTC complexes.

Effect of pH

Citric acid phosphate buffer solution was prepared by adding an appropriate volume of 0.1 mol L^{-1} citric acid to 0.2 mol L^{-1} di-sodium hydrogen phosphate solution for pH 3-8. Buffer solutions pH 2 and 9 were prepared by using 0.1 mol L^{-1} citrate buffer solution and 0.2 mol L^{-1} phosphate buffer solution, respectively, The pH of the solution was adjusted with 3 mol L^{-1} NaOH or 3 mol L^{-1} HNO_3 until to get the desirable pH.

The model solution (20 mL), containing 5.0 mg L^{-1} Cu was prepared by diluting the working solution of Cu with each pH of citric phosphate buffer solutions (pH 2-9). Each pH of their model solutions was added with 1 mL of 0.01 mol L^{-1} DDTC to form the metal-DDTC complex. After 10 min, the solution was loaded into the C_{18} cartridge. The flow of sample solution through the column was gravitationally performed. After finishing passage of the solution, the cartridge was washed with 5 mL of deionized water twice. The metals were eluted with ethanol into 20 mL volumetric flask and diluted to the mark with ethanol. For model solution of Fe and Pb were prepared and investigated as the same manner of Cu. The UV-Visible absorption spectra of these metal-DDTC complexes were recorded from 200-600 nm by running the UV Visible absorption spectrometer in scan mode.

Effect of time for complexation

This parameter was studied at 5, 7 and 10 min, respectively. The experiment was followed in the same manner as done with the effect of pH.

Effect of the eluent concentration

A 3 mol L^{-1} HNO_3 was used as an eluent, which was prepared by appropriate dilution of concentrate nitric acid with deionized water. The model solution (20 mL), containing 5.0 mg L^{-1} Fe and 2.5 mg L^{-1} Cu and Pb, was prepared by pipetting 2 mL of the working solution of Fe and 1 mL of the working solution of Cu and Pb into 20 mL volumetric flask. Then, diluted with citric phosphate buffer solution pH 6 to the mark and 5 mL of 0.01 mol L^{-1} DDTC was added. After 5 min, the solution was loaded into the cartridge. Afterward, the cartridge was washed with 5 mL of deionized water twice. The metals were recovered with various concentration of HNO_3 (1, 2, 3, 4 and 5 mol L^{-1}) into 10 mL volumetric flask and made the final volume to 10 mL. The metal concentrations in the final solution were determined by FAAS.

Effect of interfering ions

The model solutions (20 mL), containing 1.0 mg L^{-1} of Cu, Fe and Pb in citric phosphate buffer solution, were mixed with each of matrix ions; including 100 mg L^{-1} Na^+, K^+ and Mg^{2+}, 20 mg L^{-1} Li^+, Ba^{2+}, Zn^{2+}, Mn^{3+} and Al^{3+} and 2 mg L^{-1} Ni^{2+}, Cr^{3+} and Sn^{4+}, respectively. Their solution was carried out in the same procedure as described above by using 3 mol L^{-1} HNO_3 and 1.0×10^{-2} mol L^{-1} DDTC as an eluent and chelating agent, respectively.

Preparation of wine and distilled spirit samples

Wine or distilled spirit (50 mL) was evaporated in drying oven at 100 ^oC until dryness. After cooling at room temperature, the residue was treated with various volume of conc.HNO_3 or acid mixture (conc.HNO_3 and 30% H_2O_2). Afterwards, the mixture was heated on hot plate about 110 ^oC and 80 ^oC in hood for wine and distilled spirit, respectively. The mixture was therefore evaporated until dryness. Effect of sample volume was also studied. Wine and distilled spirit were prepared in the same manner as described above by various volumes in the range of 100-300 and 100-400 mL for wine and distilled spirit, respectively.

After the digested sample solution was cool down to room temperature, 10 mL of the citric phosphate solution was added to the residue and then the solution was filtered through Whatman filter paper No.41. Afterward, these solutions were adjusted to pH 6 with a dropwise of 3 mol L^{-1} NaOH solution. Then, the preconcentration procedure; using 3 mol L^{-1} HNO_3 and 1.0×10^{-2} mol L^{-1} DDTC as an eluent and chelating agent, respectively was applied to the samples (10-mL final volume) prior to FAAS measurement.

In addition, the residue of samples digested by acid was also dissolved with deionized water, then the sample solution was filtered through Whatman filter paper No.41 and made the final volume to 10 mL with deionized water prior to FAAS measurement without using the precencentration step.

Results and Discussion

Metal-DDTC complex and preconcentration

The optimized conditions including pH, reagent concentrations and matrix effect for the quantitative preconcentration were established by using model solutions. The pH of the test solutions is one of the important parameters affecting the efficiency of DDTC when reacts with metals and forms uncharged metal-DDTC complexes. Thus, this parameter was investigated in the pH range of 2-9 by employing buffer solutions according to the desired pH. As shown Figure 1, the absorbance of each metal-DDTC complex at its maximum wavelength (208 nm, 344 nm and 432 nm for Pb-DDTC, Fe-DDTC and Cu-DDTC, respectively) was plotted as a function of pH. It was found that pH in the range of 5-9, 6-7 and 6-8 was the highest absorption for Cu, Fe and Pb, respectively. Based on the results observed, the working pH was chosen at 6 to fix the compromised conditions of all three elements.

The absorbance of the DDTC complex of Cu, Fe and Pb at each maximum wavelength was plotted as a function time. It was found that absorbance was slightly different in the range of 5-10 min, indicating a complete reaction as shown in Figure 2. Therefore, the time course for their metal-DDTC complex formation was chosen within 5 min.

Since uncharged metal-DDTC complexes are adsorbed onto the adsorbent packing material in C_{18} cartridges, elution of metals must imply the metal-DDTC destruction. Previous report has shown that AAS encounter the problem of the presence of a complex organic matrix that causes severe suppression of analyte signal[35-37]. Thus, in this study, a nitric acid solution was selected for the elution of the metal ions.

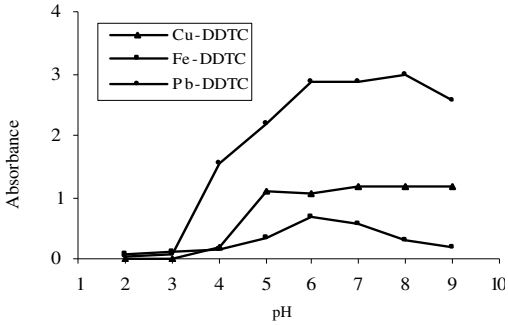

Figure 1. Effect of pH on the absorbance of metal-DDTC complex; 5 mg L^{-1} Cu, Fe and Pb (n = 6)

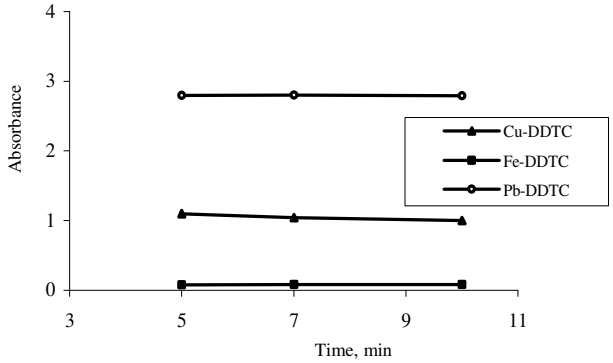

Figure 2. Effect of reaction time on the absorbance of metal-DDTC complex; 5 mgL^{-1} Cu, Fe and Pb (n = 6)

The recoveries of the metals increased with an increasing the concentration of HNO_3 and reached a constant value over 98% at 3 mol L^{-1} HNO_3 (as shown in Figure 3 and Table 1). From the results, the experimental studies were carried out using 3 mol L^{-1} HNO_3 as an eluent.

The influence of DDTC concentration on the recovery of the examined metal ions was investigated in the range of 1.0×10^{-4} – 2.0×10^{-2} mol L^{-1} using the buffered model solution containing 5 mg L^{-1} of Cu and Pb and 10 mg L^{-1} of Fe. As shown in Figure 4, the DDTC concentration is suitable in the range of 5.0×10^{-3} to 2.0×10^{-2} mol L^{-1}. Thus, the DDTC concentration of 1.0×10^{-2} mol L^{-1} was used for determination of all three elements.

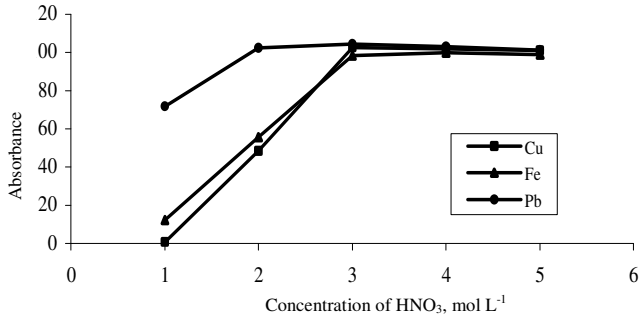

Figure 3. Effect of HNO_3 concentration as eluent on the recovery of 5 mg L^{-1} Fe and 2.5 mg L^{-1} of Cu and Pb (n = 6)

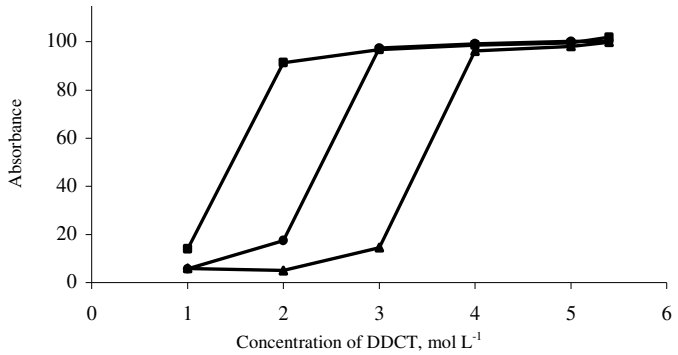

Figure 4. Effect of DDTC concentration on the recovery of 5 mg L^{-1} Fe and 2.5 mg L^{-1} of Cu and Pb (n = 6)

Table 1. Recovery of Cu, Fe and Pb determination in each fraction (10 mL) of the analyte elution (n = 6)

Concentration of HNO_3, mol L^{-1}	Effluent, analyte elution	Recovery, % ± S.D.		
		Cu	Fe	Pb
1.0	Fraction 1	0.60±0.001	12.2±0.034	71.7±0.0 62
	Fraction 2	11.7±0.012	23.5±0.029	25.0±0.048
	Fraction 3	18.5±0.019	27.9±0.016	n.d.
2.0	Fraction 1	48.4±0.017	55.6±0.033	102±0.094
	Fraction 2	44.5±0.038	42.6±0.051	N.D.
	Fraction 3	n.d.	n.d.	n.d.
3.0	Fraction 1	103±0.064	98.7±0.103	104±0.102
	Fraction 2	n.d.	n.d.	n.d.
	Fraction 3	n.d.	n.d.	n.d.
4.0	Fraction 1	102±0.028	99.4±0.091	103±0.070
	Fraction 2	n.d.	n.d.	n.d.
	Fraction 3	n.d.	n.d.	n.d.
5.0	Fraction 1	101±0.021	98.1±0.073	101±0.057
	Fraction 2	n.d.	n.d.	n.d.
	Fraction 3	n.d.	n.d.	n.d.

Model solution was used consisting of 5 mg L^{-1} Fe, and 2.5 mg L^{-1} of Cu and Pb. n.d., not detectable

Effect of interfering ions

Since determination of trace level of metal ions in local wine and distilled spirit samples is the main objective. The common problem in the FAAS determination of the trace metals is usually accounted for interferences from the matrices of samples. In this study, the influence of some interfering ions was investigated by concentration choice based on the literature values found in beverage samples. The results are summarized in Table 2, it is concluded that alkaline and alkaline earth metals are almost not retained through the SPE cartridge due to low stability constant of the DDTC used. Also, some of the transition metals at mg L^{-1} levels caused an error with less than ±5% associated with recoveries of the interested metals under the experimental conditions. This results show that the proposed preconcentration method could be applied to both wine and distilled spirit samples containing some transition metals.

Table 2. Effect of some matrix ions on the recovery of Cu, Fe and Pb (n = 5)

Ion	Added as	Ion concentration, mg L^{-1}	Recovery, % ± S.D.		
			Cu	Fe	Pb
Na^+	NaCl	100	102±0.007	106±0.007	100±0.004
K^+	KCl	100	103±0.032	97.4±0.069	99.0±0.039
Mg^{2+}	$Mg(NO_3)_2$	100	101±0.009	100±0.025	102±0.002
Li^+	$LiNO_3$	20	104±0.004	98.7±0.043	108±0.001
Ba^{2+}	$BaCl_2$	20	101±0.006	101±0.006	114±0.011
Zn^{2+}	$ZnCl_2$	20	114±0.013	105±0.054	105±0.027
Mn^{2+}	$MnCl_2$	20	105±0.013	96.9±0.007	101±0.006
Al^{3+}	$AlCl_3$	20	104±0.009	99.2±0.025	95.2±0.021
Ni^{2+}	$Ni(NO_3)_2$	2	109±0.005	110±0.015	97.8±0.026
Cr^{3+}	$Cr(NO_3)_3$	2	98.7±0.007	97.7±0.002	96.5±0.015
Sn^{4+}	$SnCl_4$	2	97.6±0.031	99.3±0.006	97.1±0.018

The model solution was used consisting of 1.0 mg L^{-1} Cu, Fe and Pb

Sample preparation

In this case preliminary evaporation of ethanol is performed in order to avoid strong bubble formation while digestion procedure proceeds and to ensure better conditions for a complete mineralization of organic matter in the sample. Wine and distilled spirit samples were treated with various volumes of acid. The results are shown in Table 3. It was found that the recoveries of Pb were quantitative (higher than 95%) for all ratios of sample: HNO_3: H_2O_2 in wine and distilled spirit samples. Some ratios of sample: HNO_3: H_2O_2 given the recoveries of Cu and Fe were lower than 95%; that is in the ratio of 10: 3: 0 for Cu in wine, 10: 3: 0.5 for Cu and Fe in wine and 50: 0: 0 for Cu and Fe in distilled spirit. From this result, the ratios of 10: 4: 0 and 50: 1: 0 were chosen for all elements determination in wine and distilled spirit samples, respectively.

Table 3. Recovery of Cu, Fe and Pb in wine and distilled spirit samples using various ratios of sample and oxidizing agent (n = 3)

Beverage	Sample: HNO_3: H_2O_2	Recovery, % ± S.D.		
		Cu	Fe	Pb
Wine	10 : 3 : 0	92.2±0.005	95.0±0.010	99.3±0.006
	10 : 4 : 0	101±0.002	100±0.027	96.6±0.022
	10 : 5 : 0	103±0.003	99.1±0.032	98.1±0.003
	10 : 3 : 0.5	94.2±0.019	91.5±0.059	98.5±0.041
	10 : 4 : 0.5	111±0.005	109±0.026	97.3±0.008
Distilled spirit	50 : 0 : 0	89.0±0.028	92.2±0.017	95.2±0.005
	50 : 1 : 0	98.2±0.002	108±0.080	97.0±0.007
	50 : 2 : 0	97.6±0.021	104±0.013	101±0.010
	50 : 3 : 0	99.3±0.021	112±0.093	98.3±0.012
	50 : 5 : 0	97.6±0.010	106±0.035	96.7±0.002

Spiked samples were contained 0.1 mg L^{-1} Cu, Fe and Pb.

The SPE technique is a common procedure for extraction and separation of ions from a large sample volume to obtain a high preconcentration factor. In this study, the influence of sample volume was investigated in the range of 50-400 mL of sample containing 0.1 mg L^{-1} of each metal ion. The results obtained from both standard curve method and standard addition method are listed in Table 4. It was found that the averaged recoveries of each

element were higher than 97.9 and 96.1% for wine and distilled spirit, respectively. Therefore, the preconcentration of these metals was not affected by the sample volume between 100-300 and 100-400 mL for wine and distilled spirit, respectively. Thus, sample volume in this range could be used in the proposed procedures.

Table 4. Effect of sample volume on recovery of Cu, Fe and Pb determination (n = 3)

Beverage	Metal	Sample volume, mL	Concentration, mg L^{-1}		Recovery, %
			Standard curve method	Standard addition method, spiked 0.1 mg L^{-1}	
Wine	Cu	100	0.040±0.001	0.142±0.008	103
		200	0.039±0.004	0.147±0.002	108
		300	0.040±0.003	0.158±0.003	118
	Fe	100	1.897±0.056	1.996±0.031	99.0
		200	1.876±0.069	1.975±0.031	98.2
		300	1.877±0.001	1.983±0.014	106
	Pb	100	n.d.	0.098±0.007	97.9
		200	n.d.	0.106±0.007	107
		300	n.d.	0.101±0.003	101
Distilled spirit	Cu	100	0.117±0.036	0.225±0.010	108
		200	0.105±0.011	0.211±0.076	106
		300	0.117±0.037	0.213±0.034	96.1
		400	0.123±0.054	0.230±0.041	104
	Fe	100	0.033±0.004	0.150±0.011	117
		200	0.031±0.008	0.133±0.008	99.8
		300	0.032±0.021	0.138±0.008	106
		400	0.035±0.021	0.136±0.015	101
	Pb	100	0.019±0.003	0.124±0.009	106
		200	0.016±0.006	0.123±0.009	107
		300	0.021±0.034	0.133±0.004	112
		400	0.022±0.011	0.124±0.010	102

n.d., not detectable

Consequently, suitable for the quantitative preconcentration by SPE of Cu, Fe and Pb in this study was using 0.01 mol L^{-1} DDTC solution and 3 mol L^{-1} HNO_3 as chelating agent and eluent, respectively. The working pH was 6 to fix the compromised conditions for complexation of all three elements with DDTC. The ratio of sample: HNO_3 for acid digestion was 10:3 and 50:1 for wine and distilled spirit sample, respectively. As shown in Table 5, good recovery for determination of model solution was contained Cu, Fe and Pb using this proposed condition.

Table 5. Determination of Cu, Fe and Pb contents using the developed method (n = 5)

Metal	Concentration, mg L^{-1}		Recovery, %
	Taken	Found ± S.D.	
Cu	0.10	0.096±0.003	96.0
	0.50	0.511±0.009	102
Fe	0.10	0.104±0.012	104
	0.50	0.498±0.018	99.6
Pb	0.10	0.102±0.025	102
	0.50	0.530±0.219	106

Analytical performance characteristics

The accuracy and precision of the overall procedures (SPE and FAAS determination) are reported in terms of recovery (%) and R.S.D.(%), respectively, by determination of various amounts of these metal ions spiked to the samples used. The result in Table 6 shows good recoveries for Cu, Fe and Pb determination of each with two spiked levels in wine and distilled spirit sample.

Table 6. Recovery of Cu, Fe and Pb in the spiked sample determined by the developed procedure (n = 3)

Sample	Metal	Concentration, mg L^{-1}		Recovery, %
		Taken	Found ± S.D.	
Wine	Cu	0.00	0.024±0.001	-
		0.05	0.072±0.006	96.5
		1.00	0.989±0.026	96.6
	Fe	0.00	0.598±0.013	-
		0.05	0.621±0.011	116
		1.00	1.613±0.008	102
	Pb	0.00	n.d.	-
		0.02	0.018±0.001	91.7
		0.50	0.510±0.007	102
Distilled spirit	Cu	0.00	0.1215±0.004	-
		0.05	0.1720±0.004	101
		1.00	1.1023±0.007	98.0
	Fe	0.00	0.0360±0.005	-
		0.05	0.0581±0.001	110
		1.00	1.0653±0.003	103
	Pb	0.00	0.0262±0.003	-
		0.02	0.0467±0.037	103
		0.50	0.5602±0.105	107

n.d., not detectable

However, the precision (R.S.D.) for 10 replicate determinations of 0.1 mg L^{-1} Cu, Fe and Pb in model solutions were 3.7, 4.2 and 7.1%, respectively. From these results, it is concluded that the procedure offers a good repeatability for all elements. The limits of detection were defined as the concentration equivalent to three times the standard deviation, n = 10, of the blank solution (3SD). The values were 0.001 mg L^{-1} for Cu, 0.003 mg L^{-1} for Fe and 0.006 mg L^{-1} for Pb. The limit of quantitation (10SD) was 0.005, 0.012 and 0.019 mg L^{-1} for Cu, Fe and Pb, respectively. The regression equation and correlation coefficient (r^2) for Cu was $y = 0.0458x + 0.0005$ and 1.0000, for Fe was $y = 0.0281x + 0.0061$ and 0.9998 and for Pb was $y = 0.0084x - 0.0003$ and 0.9994, respectively. The preconcentration factor calculated from the ratio of sample volume used in this study (150 mL) to 10 mL final volume was 15.

Table 7 shows the result of these metals determination in wine and distilled spirit samples that was prepared by acid digestion and SPE method comparing with acid digestion without SPE method using the sample of 150 mL. It was observed that precision of using the SPE method was higher than that of without using one. Especially the determination of wine sample, it was found that using SPE method is better than without using one for Cu and Pb determination, since the content of Cu and Pb in wine is quite low. For the determination of Fe

in wine sample, it was found that a slight difference in the results for both procedures was due to high Fe content in the sample used. Distilled spirit sample was slightly interfered with matrices and thus gave slightly different in the results for of both procedures. But at a very low level of metals using no SPE step these elements were not detectable, while the SPE did.

Table 7. Comparative determination of Cu, Fe and Pb contents using the developed procedure with and without SPE method (n = 3)

Sample	Metal	Procedure with SPE		Procedure without SPE	
		Conc., mg L^{-1} ± SD	R.S.D, %	Conc., mg L^{-1} ± SD	R.S.D, %
Red wine	Cu	0.012	8.4	n.d.	n.d.
	Fe	2.911	1.2	3.014	3.40
	Pb	0.052	9.6	0.032	127
White wine	Cu	0.021	9.4	0.050	82.1
	Fe	0.573	4.0	0.550	13.8
	Pb	0.007	15	n.d.	n.d.
Distilled spirit	Cu	0.135	3.7	0.153	11.2
	Fe	0.245	4.9	0.320	17.2
	Pb	0.018	11	n.d.	n.d.

n.d., not detectable

Real sample analysis

The SPE procedure for Cu, Fe and Pb with DDTC on C_{18} cartridge was applied to local thai wine and distilled spirit samples. The results are given in Table 8. The Cu contents found in wines and distilled spirits are ranged between 0.012-0.80 mg L^{-1} and 0.12-8.8 mg L^{-1}, respectively. The Fe concentration found in this study was in the range of 0.18-3.4 and 0.036-0.29 mg L^{-1} for wines and distilled spirits, respectively. That amount was lower than the upper permissible limit established by TCPS, which should be accounted at 15 mg L^{-1}.

Table 8. Determination of Cu, Fe and Pb in fruit wine and distilled spirit samples (n = 3)

Sample	Concentration, mg L^{-1} ± SD		
	Cu	Fe	Pb
RW 01	0.047 ±0.004	0.74±0.001	0.034±0.005
RW 02	0.084±0.002	0.72±0.003	0.0070±0.004
RW 03	0.022±0.008	2.5±0.017	n.d.
RW 04	0.039±0.001	1.9±0.891	n.d.
RW 05	0.049±0.005	1.1±0.028	0.012±0.002
WW 01	0.012±0.005	3.4±0.153	n.d.
WW 02	0.80±0.049	1.7±0.008	0.053±0.001
WW 03	0.11±0.023	1.6±0.254	0.017±0.002
WW 04	n.d.	0.24±0.031	0.0090±0.001
WW 05	0.055±0.011	0.18±0.021	n.d.
DS 01	0.12±0.004	0.036±0.007	0.026±0.003
DS 02	8.8±0.102	0.12±0.088	n.d.
DS 03	0.18±0.006	0.10±0.018	0.018±0.004
DS 04	1.6±0.053	0.29±0.049	n.d.
DS 05	0.33±0.008	0.076±0.005	n.d.

n.d., not detectable

All analyzed wine and distilled spirit samples contained Pb contents lower than the upper value of TCPS, permissible limit is 0.2 mg L^{-1}. In this study, Pb concentrations in wines were in the range of 0.0074 - 0.053 mg L^{-1}, while Pb concentration in distilled spirits were in the range of 0.014 - 0.026 mg L^{-1}. The Pb concentrations in some samples were not detectable due to it was lower than the method detection limit.

Conclusion

Copper, iron and lead determinations, based on acid digestion of sample and subsequent SPE, were investigated. The ratios of sample: conc. HNO_3 that used for wine and distilled spirit digestion were 10:4 and 50:1 by volume, respectively. Optimized SPE conditions; 0.01 mol L^{-1} DDTC solution was added to digested sample for complexation. Then the complexes was sorbed onto C_{18} cartridge and eluted with 3 mol L^{-1} HNO_3 that is adequate for preconcentration and separation of some interfering ions prior to FAAS measurement. Some interference ions caused an error with less than $\pm$5% associated with recoveries of the metal ions under the experimental conditions used. It is concluded that the proposed procedure, besides providing an increase in both sensitivity and selectivity, allows the separation of the interfering matrix, so that external calibration can be used resulting in a high precision. Based on the results at the highest concentration of Cu, Fe and Pb in these samples can be calculated, suggesting an adequate intake in every day's life of alcoholic beverages.

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