



SOLIDIFIED FLOATING ORGANIC DROP MICROEXTRACTION– ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF TRACE AMOUNTS OF LEAD IN WATER SAMPLES

(Pengekstrakan Mikro Pemejalan Titisan Organik Terapung-Spektrometri Serapan Atom
Elektrotermal bagi Penentuan Jumlah Surih Plumbum di dalam Sampel Air)

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Abstract

Solidified floating organic drop microextraction (SFODME) was utilized as a separation or pre-concentration step prior to electrothermal atomic absorption spectrometric (ETAAS) determination of ultra-trace amounts of lead. The method was based on the formation of an extractable complex between Pb(II) and 1-(2-pyridylazo)-2-naphthol (PAN) as a chelating agent. The main parameters affecting the performance of SFODME, namely, type and volume of organic solvent, pH, concentration of the chelating agent, extraction time, stirring rate, extraction temperature, disperser solvent, ionic strength, and interference effect were investigated and optimized. Under optimized experimental conditions a pre-concentration factor of 22.03 and a detection limit of $0.064 \mu\text{g L}^{-1}$ for the pre-concentration from 13.0 mL water sample was achieved. The relative standard deviation of the measurements in the range of 1.3 – 2.5% ($n = 6$). The proposed method was assessed through the analysis of certified reference water and recovery experiment with satisfactory results.

Keywords: solidified floating organic drop microextraction, lead, electrothermal atomic absorption spectrometry, water samples

Abstract

Pengekstrakan mikro pemejalan titisan organik terapung (SFODME) digunakan sebagai langkah pemisahan atau pemekatan sebelum penentuan jumlah surih plumbum ditentukan menggunakan spektrometri serapan atom elektrotermal (ETAAS). Kaedah ini berasaskan kepada pembentukan kompleks yang boleh diekstrak di antara Pb(II) dan 1-(2-piridilazo)-2-naphthol (PAN) sebagai agen pengkelat. Parameter utama yang memberi kesan kepada prestasi SFODME iaitu jenis dan isipadu pelarut organik, pH, kepekatan agen pengkelat, masa pengekstrakan, kesan pengacauan, suhu pengekstrakan, pelarut serakan, kekuatan ionik dan kesan gangguan telah dikaji dan dioptimumkan. Keadaan optimum bagi eksperimen diperolehi dengan faktor pemekatan pada 22.03 dan had pengesanan dicapai pada $0.064 \mu\text{g L}^{-1}$ bagi pemekatan 13.0 mL sampel air. Pengukuran sisihan piawai relatif berada pada julat 1.3 – 2.5% ($n = 6$). Kaedah yang dicadangkan juga dinilai melalui analisis sampel air rujukan yang disahkan dan ujian perolehan semula yang mencapai keputusan memuaskan.

Kata kunci: pengekstrakan mikro pemejalan titisan organik terapung, plumbum, spektrometri serapan atom elektrotermal, sampel air

Introduction

Nowadays, increasing global environmental pollution is great concern. Heavy metals belong to a class of pollutants that can produce undesirable effects, even if they are present in minuscule amounts. Among the different heavy metals, lead is one of the most common and most toxic pollutants released into the environment from various industrial activities [1]. The accumulation of heavy metals in adults, is associated with heart disease, cancer, and may cause many serious disorders like anemia, kidney diseases, nervous disorder, and even death [2].

The important sources of lead are industrial processes such as smelting of lead, recycling of lead batteries, manufacturing of lead paints, etc. [3], and automobile exhausts. Water quality has become an issue of vital importance as it is an essential resource that is threatened by pollution. Maximum allowable limit of total Pb in drinking water considered safe by the United States Environmental Protection Agency (EPA) and Ministry of public health, Thailand is $10 \mu\text{g L}^{-1}$ [4]. The tap water intended for human consumption is controlled regularly for an extensive array of potential contaminants by certified authorities.

Modern instrumental methods including spectrometry, namely, inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry, and atomic absorption spectrometry, etc. [5-7] have been used for the determination of traces of metal ions in various media. However, because of the low concentration of Pb and the complexity of the environmental samples, direct analysis using the instruments is often impeded by matrix interferences. Several methods have been proposed for separation and pre-concentration of trace Pb, such as, liquid-liquid extraction (LLE) [8, 9], solid-phase extraction (SPE) [10-12], coprecipitation [13], cloud point extraction (CPE) [14, 15], and ion exchange [16]. Although these are the most commonly used sample pre-treatment methods, they have some drawbacks such as large consumption of reagents, low enrichment factors, multistage operation, and lengthy separation.

The miniaturized pre-concentration method based on LLE including, single drop microextraction (SDME) [17], hollow fiber liquid phase microextraction (HF-LPME) [18], homogeneous liquid-liquid extraction [19], and dispersive liquid-liquid microextraction (DLLME) [20, 21]. Solidified floating organic drop microextraction (SFODME) was introduced as one of these by Khalili Zanjini et al. [22]. In this method, a small volume of an organic solvent with a melting point near room temperature (in the range of 10-30 °C), which is immiscible with water, is delivered to the surface of an aqueous sample containing the analytes. When the equilibrium is reached, the sample vial is placed in an ice bath to solidify the microdrop which is easily removed and allowed to melt for the quantification of analytes [23].

In the present work, trace analysis of lead was developed based on SFODME technique and determination by electrothermal atomic absorption spectrometry (ETASS). 1-(2-pyridylazo)-2-naphthol (PAN), a chelating reagent widely used for many metals and that permits the pre-concentration of trace metals from solution [24], is used to extract Pb into the organic phase. This method was applied for the determination of lead in mineral bottled and tap water samples.

Materials and Methods

Instrumentation

The experiments were performed with a Varian Model SpectraAA 220Z atomic absorption spectrometer equipped with Zeeman background correction. A lead hollow cathode lamp was used as the radiation source. The analytical wavelength (283.3 nm), spectral bandwidth (0.5 nm) and lamp current (10.0 mA) were used as recommended by manufacturer. The graphite furnace temperature program was optimized and are showed in Table 1. The pH measurements were carried out with a Metrohm pH meter model 827 pH lab equipped with a combined glass electrode.

Reagents and solutions

All reagents used in this study were of analytical grade. The stock solution of Pb(II) was obtained from AVS Titrimorm (VWR inter-national, Belgium). Working standard solutions were prepared daily by appropriate dilution from the stock solution with deionized water. The stock solutions of the chelating agent, 1-(2-pyridylazo)-2-

naphthol; PAN, (Acros organics, USA) were prepared by dissolving appropriate amounts in ethanol (ITALMAR, Thailand). The extraction solvent, 1-undecanol, was purchased from Merck, Germany. Buffer solutions of ammonium acetate (pH 4, 0.2 mol L⁻¹), phosphate (pH 7.0, 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 2.0-12.0. The laboratory glassware was kept overnight in a 10% HNO₃ solution. The glassware was washed with deionized water and dried prior to use.

Table 1. Temperature program of ETAAS for determination of Pb

Step	Temperature (°C)	Time (s)	Argon flow rate (L/min)
1	95	15.0	0.3
2	120	5.0	0.3
3	400	14.0	0.3
4	2100	2.9	0
5	2100	2.0	0.3

Extraction procedure

An amount of 13 mL aliquot, either 15 µg L⁻¹ standard or water sample, was placed in a 15-mL screw cap glass vial with flat bottom containing a magnetic stirrer bar. The pH of the solution was adjusted to 6 using phosphate buffer and 0.5 mL of a solution of PAN chelating agent (3.0 mmol L⁻¹) was added. After the solution was mixed thoroughly, 90 µL of 1-undecanol was spiked into the stirring solution and was mixed for 20 min at 625 rpm, after that, the vial was cooled in an ice bath. The solidified drop of 1-undecanol was obtained rapidly. The solidified solvent was transferred into a vial and where it melted immediately. Therefore, the extract was diluted with ethanol (500 µL) and Pb(II) concentration was determined by electrothermal atomic absorption spectrometer.

Water samples

In order to validate the method, various water samples, including tap and mineral bottled water (Phitsanulok, Thailand) were selected. A water samples were filtered through a 0.45 µm Whatman filter membrane to remove any suspended material prior to the analysis.

Results and Discussion

Optimization of extraction conditions

In order to obtain high pre-concentration factor (PF) [25] and good extraction recovery (ER), the effect of different parameters that affect extraction conditions such as type and volume of extraction solvent, pH, amount of chelating agent, stirring rate, extraction time and extraction temperature were optimized.

Effect of type and volume of the extraction solvent

To obtain optimal results, an appropriate extraction solvent must be chosen. It should have low volatility, density lower than water, low toxicity, and a melting point near room temperature (10 – 30 °C). In this paper, 1-undecanol (m.p. 13–15 °C) and 1-dodecanol (m.p. 22–24 °C), were used for the initial investigation. When the extraction was done, the analytical absorbances were about 0.071 and 0.034, respectively. Therefore, 1-undecanol was selected as the extraction solvent for further experiment in this study.

To evaluate the effect of the extraction solvent volume, different volumes of 1-undecanol were added in the range of 20 – 150 µL. The results of this experiment are shown in Figure 1. It can be seen that relative absorbance increased with increasing 1-undecanol volume in the range of 20 – 90 µL, and then decreased with further volume increases. Therefore, 90 µL was chosen as the optimum volume of the extraction solvent for further experiments. After the extraction procedure, the obtained of PF was 22.03.

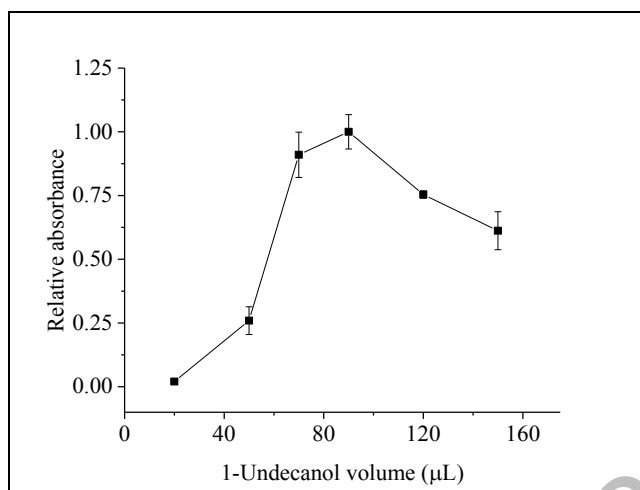


Figure 1. Effect of 1-undecanol volume on the extraction efficiency of lead. Utilized conditions: concentration of Pb(II), $15 \mu\text{g L}^{-1}$; aqueous volume, 13 mL; pH 6; chelating agent, PAN, 3.0 mmol L^{-1} , 0.5 mL; extraction time, 3 min; stirring rate, 625 rpm; room temperature

Effect of the sample pH

The pH of the sample has an effect on metal complex formation. Furthermore, pH also has influences toward the extraction efficiency of Pb(II). Therefore, the effect of pH on the procedure was investigated in the range of 3.0-12.0. As shown in Figure 2, an absorbance maximum was observed pH equal to 9.0. Accordingly, a pH 9, obtained with ammonium chloride buffer, was selected for the optimization studies and real sample analysis.

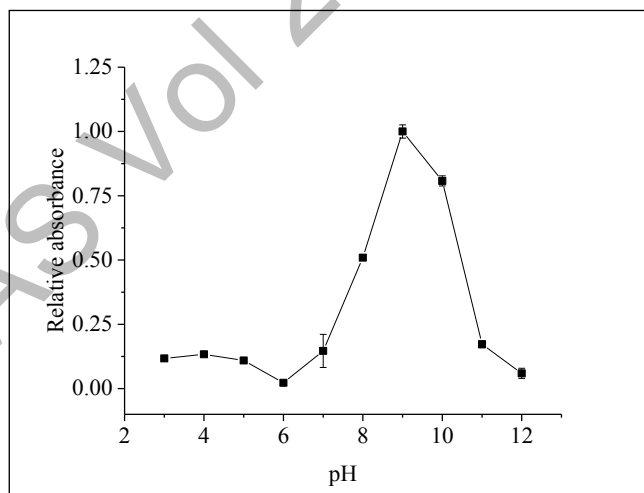


Figure 2. Effect of pH on the extraction efficiency of lead. Conditions are the same as in Figure 1 except pH, and 1-undecanol volume, 90 μL

Effect of the PAN concentration

The effect of PAN concentration, as chelating reagent, on the extraction efficiency was studied using various amounts of ligand ranging from 0.1 to 10.0 mmol L^{-1} (equal 0.0038 to 0.38 mmol L^{-1} in final volume of sample, 13

mL). The absorbance was stable when the concentration of ligand was higher than 3.0 mmol L^{-1} , indicating the complete complexation. Therefore, 3.0 mmol L^{-1} (equal $0.115 \text{ mmol L}^{-1}$ in final solution) was chosen as the optimum concentration for the lead extraction.

Extraction time

Another important factor that affects the extraction is the extraction time, because of the mass transfer phenomena governing the extraction efficiency of the analyte in SFODME. The effect of the extraction time was studied by varying it in the range of 10 – 120 min under constant experimental conditions. The results are shown in Figure 3. It was found that with increasing extraction time, up to 40 min, the analytical signal increased, and remained constant at a longer extraction times. Thus, 40-min extraction was chosen as the optimum extraction time.

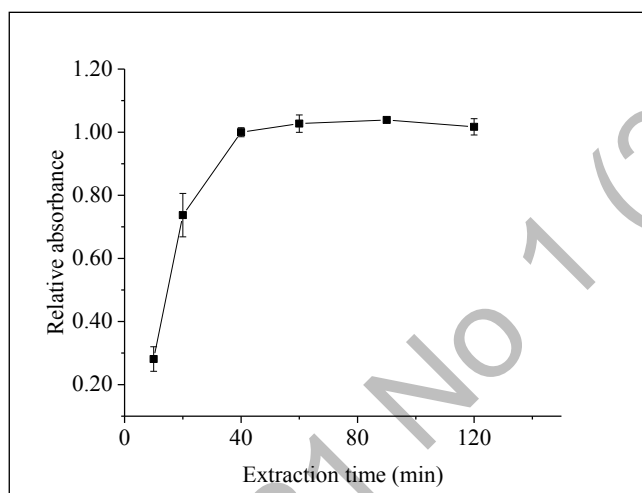


Figure 3. Effect of extraction time on the extraction efficiency of lead. Conditions are the same as in Figure 2 except extraction time. Performed at pH 9

Stirring rate

To enhance the extraction efficiency, sample stirring during the extraction procedure was applied. Based on the film theory of convective-diffusive mass transfer, increasing the stirring rate can decrease the thickness of the dilution film in the aqueous phase, so the mass-transfer will be increased. The effect of stirring rate on extraction efficiency was studied in the range of 100 – 1,200 rpm. The experimental results show that the analytical signal increases rapidly with increasing stirring rate from 375 to 750 rpm, and then remains constant upon further increases up to 1200 rpm. Therefore, a stirring rate of 750 rpm was employed for analysis.

Extraction temperature

Temperature affects the solubility of the organic solvent in water as well as the emulsification and therefore influences the extraction efficiency. This effect was performed by varying the extraction temperature between 20°C and 80°C . The results in Figure 4 showed that the relative absorbance increases with increasing extraction temperature up to 50°C . At temperatures higher than 50°C , 1-undecanol was slightly dissolved into the aqueous sample, affecting the analytical signal. Consequently, the extraction temperature at 50°C was chosen for further study.

Effect of salts

The influence of ionic strength on the SFODME method was investigated by adding various amounts of sodium chloride (NaCl) and potassium chloride (KCl) in the range 0 – 5.0% (m/v) to the sample. The obtained results indicate that increasing the salt concentration from 0% to 5.0% does not significantly increase the extraction efficiency. Therefore, salts were not added to the aqueous samples studied in this work.

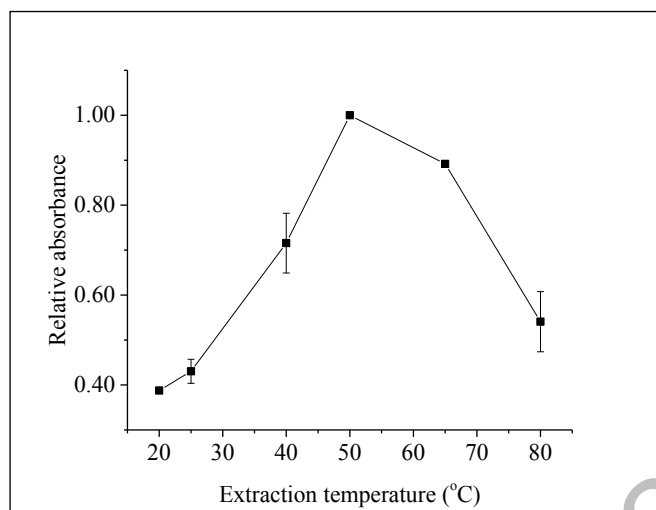


Figure 4. Effect of extraction temperature on the extraction efficiency of lead. Conditions are the same as in Figure 3 except extraction temperature. Performed with extraction time of 40 min

A summary of optimal conditions obtained for the SFODME method for pre-concentration and determination of lead is illustrated in Table 2.

Table 2. Optimal conditions for SFODME of lead ions

Optimal Conditions for SFODME of Pb(II)	
Extraction solvent	1-undecanol
Diluent	ethanol
pH	9
PAN concentration (mmol L ⁻¹)	3.0
Extraction time (min)	40
Stirring rate (rpm)	750
Sample volume (mL)	13
Extraction phase volume (mL)	0.090
Extraction temperature (°C)	50

Interference study

The selectivity of the proposed method in the extraction and determination of the analyte was investigated as well. In these experiments, solutions of 10 µg L⁻¹ of Pb(II) containing interfering ions were treated using the optimized procedure. The tolerance limit was set as the amount of ion required to cause an error of ±5% in the determination of lead. The maximum tolerance limits of the investigated cations and anions are given in Table 3. The extraction by SFODME method is based on the fact that the target ions can form hydrophobic metal–PAN complex and them can be extracted to the extraction solvent (1-undecanol). Nonetheless, the tolerance limits of Mg²⁺ and Fe³⁺ were not as high as other ions, the concentration of Mg²⁺ and Fe³⁺ were at trace levels in several water samples. Therefore, these results indicate that the developed method can be applied to analysis of Pb in various water samples.

Table 3. Tolerance limits of interfering ions in the determination of 10 $\mu\text{g L}^{-1}$ Pb(II)

Ions	Interfering Ratio (ion/Pb)	Pb(II) Recovery (% $\pm$ SD)
Na ⁺	1000	103.0 $\pm$ 0.1
K ⁺	1000	94.9 $\pm$ 0.2
Cd ²⁺	100	94.2 $\pm$ 0.3
Cr ³⁺	1000	97.9 $\pm$ 0.1
As ³⁺	100	92.4 $\pm$ 0.1
NO ₃ ⁻	100	101.8 $\pm$ 0.1
SO ₄ ²⁻	100	100.5 $\pm$ 0.2
PO ₄ ³⁻	100	102.5 $\pm$ 0.1

Analytical performance

The analytical characteristics such as the linear range, precision, detection limit, and pre-concentration factor were obtained by processing standard solution of Pb. The calibration curve was obtained using the optimized conditions for the SFODME procedure followed by lead concentration determination by ETAAS. Linearity was obtained with lead concentration in the range up to 30.0 $\mu\text{g L}^{-1}$. The regression equation for lead determination is express as below

$$A = 0.0131C + 0.0100 \quad (1)$$

where A is the absorbance and C is the lead concentration in solution ($\mu\text{g L}^{-1}$). The correlation coefficient of the calibration curve equation was higher than 0.99. The pre-concentration factor was calculated as the ratio of the volume of the sample prior pre-concentration divided by the volume after pre-concentration. It was found to have a value of 22.03. The LOD and LOQ defined as $3S_b/m$ and $10S_b/m$ (where S_b is standard deviation of the blank and m is the slope of the calibration graph) were found to be 0.064 and 0.214 $\mu\text{g/L}$, respectively. The relative standard deviation (%RSD) for 6 replicate determinations at 15 $\mu\text{g L}^{-1}$ of Pb(II) is $\pm 2.5\%$.

Sample analysis

To examine the reliability of this procedure, the method was applied for the determination of lead in mineral bottled and tap water samples. The accuracy of the proposed method was verified by spiking experiments at two concentration levels. As tabulated in Table 4, the recoveries of the added lead were always higher than 91%. To verify the accuracy of the proposed procedure, the method was used for the determination of lead in a sample of NRC-CNRC, National Research Council of Canada (SLRS-4). The results of this test are presented in Table 4, good agreement between the determined and certified values was obtained. Furthermore, these results indicate that the matrices of the mineral bottled and tap water samples had little effect on the SFODME–ETAAS method for the determination of lead. Comparison of pre-concentration techniques used for lead determination with ETAAS was showed in Table 5.

Table 4. Determination of lead(II) in several water samples. (n=2)

Sample	Certified ($\mu\text{g L}^{-1}$)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
SLRS-4 (River water)	0.086 $\pm$ 0.007	-	0.090 $\pm$ 0.019	105.0 $\pm$ 1.9
Drinking water1		0.0	0.7 $\pm$ 0.2	-
		5.0	5.6 $\pm$ 0.1	97.0 $\pm$ 0.1
		15.0	15.3 $\pm$ 0.1	97.6 $\pm$ 2.5

Table 4 (cont'd). Determination of lead(II) in several water samples. (n=2)

Sample	Certified ($\mu\text{g L}^{-1}$)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Drinking water 2		0.0	ND*	-
		5.0	4.7 ± 0.1	94.8 ± 1.3
		15.0	15.3 ± 0.2	102.1 ± 1.9
Drinking water 3		0.0	ND*	-
		5.0	5.2 ± 0.3	103.7 ± 1.3
		15.0	12.4 ± 0.2	82.7 ± 5.7
Drinking water 4		0.0	1.56 ± 0.3	-
		5.0	6.8 ± 0.2	105.9 ± 1.9
		15.0	16.9 ± 0.3	102.2 ± 3.6
Drinking water 5		0.0	1.8 ± 0.1	-
		5.0	6.8 ± 0.1	101.0 ± 1.4
		15.0	15.2 ± 0.2	89.4 ± 2.5
Tap water 1		0.0	ND*	-
		10.0	10.2 ± 0.2	101.1 ± 2.3
		20.0	21.5 ± 0.5	107.4 ± 2.4
Tap water 2		0.0	1.9 ± 0.1	-
		10.0	12.0 ± 0.4	100.6 ± 1.9
		20.0	21.6 ± 0.4	98.1 ± 4.4
Tap water 3		0.0	2.9 ± 0.2	-
		10.0	12.0 ± 0.4	91.5 ± 1.9
		20.0	21.6 ± 0.4	93.6 ± 4.0
Tap water 4		0.0	0.3 ± 0.1	-
		10.0	10.5 ± 0.1	102.5 ± 1.2
		20.0	20.2 ± 0.4	99.6 ± 1.8
Tap water 5		0.0	1.3 ± 0.3	-
		10.0	12.0 ± 0.2	107.1 ± 0.9
		20.0	21.0 ± 0.2	98.8 ± 1.7

*N.D.: Not detected

Table 5. Comparison of pre-concentration techniques used for lead determination with ETAAS

Analytical Technique	Chelating Reagent	Sample Volume (mL)	Linear Range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	%RSD	PF	Reference
Batch-CPE	5-Br-PADAP	10.0	Up to 30.0	0.08	2.8	50	[26]
Batch-DLLME	DDTP	5.0	0.05 – 1.0	0.02	2.5	150	[27]
On-line-SPE	PSTH-cpg	3.3	0.1 – 10.0	0.012	3.2	20.5	[12]
SFODME	PAN	13.0	0.0 – 30.0	0.064	2.48	22.03	This work

PF: pre-concentration factor

Conclusion

It has been shown that solidified floating organic drop microextraction (SFODME) combined with ETAAS, can be used for the separation or pre-concentration of ultra-trace amount of lead in mineral bottled and tap water samples. A comparison of the represented method with the other liquid–liquid microextraction methods using different detection techniques for lead extraction and determination was successfully identified. It can be seen that the working range of SFODME-ETAAS is wider than that of the other reported methods. The main advantages of this methodology are simplicity, low cost, high enrichment factor, rejection of matrix constituents, and minimum use of organic solvents. Additional studies are in progress to evaluate the parameters of the SFODME method for pre-concentration and determination of other metals using various ligands and complexing agents in different matrices.

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