JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Solvent Microextraction−Flame Atomic Absorption Spectrometry (SME−FAAS) for Determination of Ultratrace Amounts of Cadmium in Meat and Fish Samples

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A simple, low cost and highly sensitive method based on solvent microextraction (SME) for separation/preconcentration and flame atomic absorption spectrometry (FAAS) was proposed for the determination of ultratrace amounts of cadmium in meat and fish samples. The analytical procedure involved the formation of a hydrophobic complex by mixing the analyte solution with an ammonium pyrrolidinedithiocarbamate (APDC) solution. In suitable conditions, the complex of cadmium−APDC entered the micro organic phase, and thus, separation of the analyte from the matrix was achieved. Under optimal chemical and instrumental conditions, a detection limit (3σ) of 0.8 ng L^{-1} and an enrichment factor of 93 were achieved. The relative standard deviation for the method was found to be 2.2% for Cd. The interference effects of some anions and cations were also investigated. The developed method has been applied to the determination of trace Cd in meat and fish samples.

KEYWORDS: Ammonium pyrrolidinedithiocarbamate; solvent microextraction; cadmium; flame atomic absorption spectrometry

INTRODUCTION

Cadmium is an element that occurs naturally in the earth's crust. Exposure to cadmium happens mostly in the workplace where cadmium products are made. Food and cigarette smoke are the largest potential sources of cadmium exposure for members of the general population. Cadmium remains in the body for a very long period. Although a lack of nickel has not been found to affect the health of humans, a small amount of nickel is probably also essential for humans. Foodstuffs naturally contain small amounts of nickel. The tobacco plant contains cadmium and nickel, most probably absorbed from the soil, fertilizing products, and pesticides. Thus, the determination of trace amounts of these metals in various matrix samples is very important in several fields, such as environmental analysis, food control, and toxicology (*1*−*3*). Also, cadmium exists broadly in the environment (*4*−*13*). It is severely dangerous to animals and humans. Cadmium mainly distributes in animal livers and kidneys. It impairs the liver, kidney, spleen, and so forth and induces immune suppression and cancer. There are some reports about the determination of cadmium by electrothermal atomic absorption spectrometry (*14*−*20*). Because of frequent low concentrations of metals in numerous samples, the determination of these elements generally is associated with preconcentration steps. Moreover, since high levels of major components usually accompany analytes, a separation step is often required. Some enrichment procedures have been developed for metal determination involving different analytical techniques such as precipitation (*21*), liquid−liquid (*22*), cloud-point (*23, 24*) or solid-phase extraction (*25*−*28*). Solid-phase extraction (SPE) has been extensively used for separation and determination of trace elements because this approach offers a number of important benefits, such as reduction of disposal costs, achievement of high recoveries, and easy recovery of the solid phase. SPE also offers a broader range of applications than liquid−liquid extraction because of the large choice of solid sorbents. Solvent microextraction is a type of liquid−liquid extraction in which the analyte partitions between the bulk aqueous phase and a very small volume of organic solvent. This relatively new technique has been described in several papers and was found to be a powerful tool for the analysis of different groups of analytes, such as alcohols (*29*), nitroaromatic explosives (*30, 31*), chlorobenzenes (*32*), drugs (*33, 34*), volatile organic compounds (VOCs) (*35*), and pesticides (*36*−*38*). SME is a very inexpensive tool that requires only common laboratory equipment and 1−100 μL of organic solvent, and it does not suffer from carryover between extractions that may be experienced when using solid phase microextraction (SPME). Other advantages of SME include simplicity, speed and potential for easy automation. To date, the potential of microextraction techniques has yet to be fully exploited, in both methodology and application (*39*−*41*).

The purpose of this work was to develop an analytical, sensitive, and simple method for the determination of trace cadmium in meat and fish by flame atomic absorption spectrometry after solvent microextraction−preconcentration. Also,

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10.1021/jf8027057 CCC: $40.75
Published on Web 01/12/2009

ammonium pyrrolidinedithiocarbamate (APDC) was used as a complexing agent.

EXPERIMENTAL PROCEDURES

Instrumentation. All measurements were carried out using a Shimadzo 170-A atomic absorption spectrometer equipped with a cadmium hollow-cathode lamp for Cd operated at 4 mA with a spectral bandwidth of 0.7 nm. The selected wavelength was 228.8 nm for Cd. In order to obtain the maximum absorbance signal, acetylene flow rate and burner height were adjusted during aspiration of the analyte solution. An M2P microbalance (Sartorius, Göttingen, Germany) with an accuracy of 0.0001 mg was used for weighing the samples.

Reagents. Analytical grade reagents were used throughout. The nitric acid (Merck, Germany) used in this work was further purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany). Distilled, deionized water with a specific resistivity of 18 MΩ cm, from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for the preparation of samples and standards. All containers and glassware were soaked in 3 mol L^{-1} nitric acid for at least 24 h and rinsed three times with water before use. Cadmium stock solution (1000 mg L^{-1}) was prepared from Titrisol concentrates (Merck). The working standards were prepared by serial dilution of the stock solutions with the addition of 0.014 mol L^{-1} nitric acid (Merck, Germany). The following reagents were used for sample digestion: %30 hydrogen peroxide (H_2O_2) and purified nitric acid (HNO_3) (both from Merck, Germany). APDC and organic solvents were purchased from Fluka. Diluted nitric acid, ammonia, and sodium hydroxide solutions were employed to adjust the pH of the standard and sample solutions.

Digestion. The reference method for digestion was the one recommended by the Brazilian Ministry of Agriculture (No. 400/03) for the determination of trace metals in muscle, liver, and kidney. 1.0000 g of fresh meat or fish samples, after being ground in a blender, was weighed in triplicate directly into 50 mL glass tubes; 5 mL of concentrated nitric acid was added and heated in a digester block to 90 °C for 1 h. The flasks were softly agitated manually to avoid foam formation. After cooling overnight, 2.0 mL of H_2O_2 was added and the mixture heated to 90 °C for 1 h. The digestion was complete when all fat of the sample had dissolved. After cooling, the volume was completed to 15 mL with water for subsequent analysis. The samples were analyzed at least three times by flame atomic absorption spectrometry after its preconcentration using the solvent microextraction method. The analyte concentration was calculated as mg kg^{-1} of the fresh meat.

Procedure. An 80 μL drop of 1-octanol was used as the extraction solvent and immersed in the stirred 60 mL aqueous sample solution for a 30 min extraction time at 35 °C. The sample solution was stirred at a rate of approximately 450 rpm using a PTFE stir bar. For all quantification experiments, the same amount of internal standard solution (Fe^{3+}) was added to the aqueous samples prior extraction. After separation of the organic phase from the aqueous phase, the solution must be diluted to 0.8 mL by ethanolic solution of 0.1 mol L^{-1} HNO_3. The final solution was introduced into an air acetylene flame by conventional aspiration for the determination of Cd and Fe. The final signal of the experiment was obtained from an absorbance ratio of these elements.

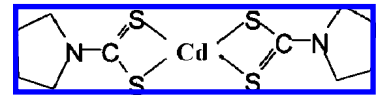
RESULTS AND DISCUSSION

SME is based on the partition of analytes between two immiscible liquid phases; often, a nonpolar organic solvent is used to extract the analytes of interest from an aqueous solution. Extracting polar organic compounds, i.e., phenolic compounds, then becomes rather more difficult as they tend to stay in aqueous media. Furthermore, headspace SME seems to be an inefficient method because of the low volatility of analytes with polar characteristics. The feasibility of an immersed SME method was, therefore, considered in order to bring the extracting phase in direct contact with the analytes, enhancing the overall mass-transfer coefficient with respect to the organic phase, β_o, an influential factor affecting the observed rate constant (S^{-1}) given by

$$k = A_i \beta_o \left(\frac{K}{V_{aq}} + \frac{1}{V_o} \right) \quad (1)$$

where A_i is the interfacial area, K the distribution constant, and V_{aq} and V_o the volumes of the organic and aqueous phases, respectively (*6*, *31*). Clearly, the higher β_o value is an indication of higher efficiency for the extraction process. According to this equation and the film theory convective diffusive mass transfer (*40*), an immersed SME method for the preconcentration of organic compounds from aqueous samples looked quite promising.

Optimization. A univariate approach was employed to optimize influential factors in this method. Various parameters affecting the SME efficiency including the type of solvent, stirring rate, extraction time, temperature of sample solution, and ionic strength were optimized. The ratio of peak area of cadmium and that of the internal standard (metallic ion) was used to assess the extraction efficiency under various conditions. For all quantification experiments, the same amount of Fe^{3+} solution was added to the aqueous samples as the internal standard. Enrichment factor defined as the ratio of the FAAS response after extraction and the one prior to extraction was used for all quantitative analysis. APDC can make a stable complex with cadmium (see below structure) and then extracted into an organic solvent.



Solvent Selection. The first step in the optimization procedure was to select an appropriate extraction solvent. The extraction solvent must satisfy the following four requirements: (1) it should possess a low volatility, (2) it should conveniently extract the analytes, (3) its absorbance peak should be well separated from the analyte peaks experiment, and (4) it should be immiscible with water. Thus, choosing the most suitable extracting solvent is very important for achieving good sensitivity, precision, and selectivity of the target compounds. Five water-immiscible solvents, namely, 1-octanol, decane, cyclohexane, butyl acetate and toluene were examined in order to find the most suitable solvent for extraction. Solvent selectivity was evaluated for the extraction of 60 mL of sample containing 20 parts per billion (ppb) of cadmium. The solution containing 80 μL of appropriate organic solvent was stirred (450 rpm) at 35 °C for 30 min. Results are given in **Figure 1**. The extraction efficiency was based on the average peak area of analyte for three replicate analyses. Apparently, 1-octanol was found to provide higher extraction efficiency. The primary reason may be attributed to the suitable polarity of 1-octanol for favor interaction with the Cd $(APDC)_2$ complex and its extraction from aqueous solution. This complex is a relatively nonpolar compound. Some solvents such as butyl acetate are polar than octanol and have a week interaction with complex, so extraction efficiency is decreased. However, if solvent hydrophobicity is increased (compared to the polarity of analyte), the interaction of complex with the solvent (such as decane) is decreased, and therefore, the extraction efficiency for this complex is reduced (**Figure 1**). Four other solvents were used in this study and were excluded from further investigation, including cyclohexane, decane, butyl acetate, and toluene. Therefore, we used octanol as the extractant solvent in this work.

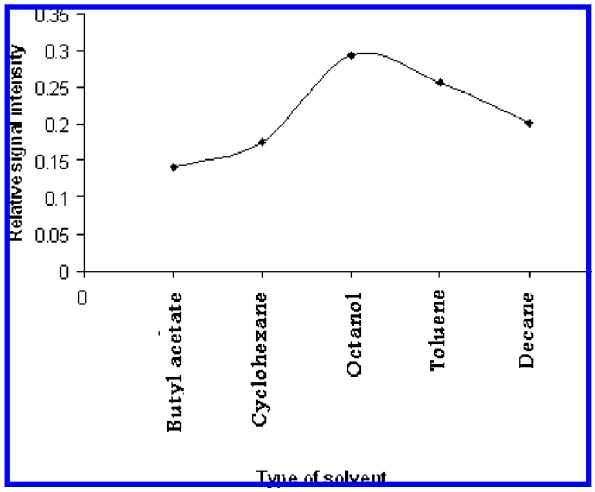


Figure 1. Effect of type of solvent on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; temperature of 35 °C; APDC 0.05% (m/v).

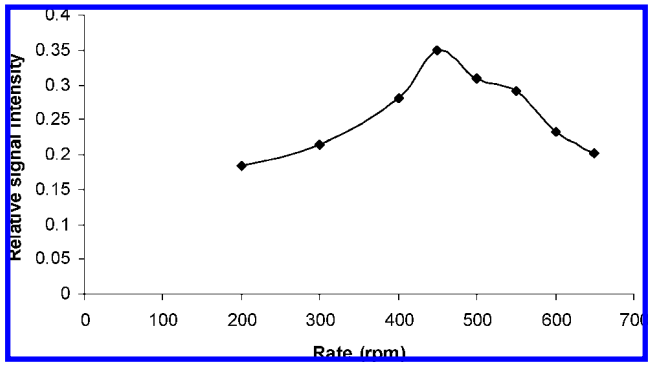


Figure 2. Effect of the stirring rate on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C; APDC 0.05% (m/v).

Stirring Rate. Sample agitation enhances extraction efficiency and reduces extraction time, especially for higher molecular mass analytes (*42*). For the purpose of the present study, three replicate analyses were taken at different stirring rates: 200, 300, 400, 450, 500, 550, 600, and 650 rpm. Faster stirring rates were avoided as they resulted in dispersing of the organic drop from the sample vial. Thus, for all further experiments, a stirring rate of 450 rpm was used. Using a small magnet with consistent stirring rate and avoiding any temperature convection were quite essential for achieving an acceptable precision. In all cases, the 80 μL 1-octanol drop was exposed at 35 °C for 30 min to a 60 mL water sample containing 20 ppb of analyte. **Figure 2** shows that the agitation significantly improves the extraction efficiencies of the cadmium.

Extraction Time. Extraction time is a major parameter affecting the extraction efficiency. SME is equilibrium, rather than an exhaustive, extraction technique and, therefore, the amount of analyte transferred into the microdrop reaches its maximum when this equilibrium is established. Thus, the procedure requires a period of time to reach equilibrium. This effect was studied in the range of 5−45 min at room temperature keeping the stirring rate constant at 450 rpm. A cadmium sample was prepared, and the variation of the analytical signal for Cd was studied as a function of exposure time. **Figure 3** shows that the analytical signal increases quickly with increasing extraction time in the range of 5−45 min, and after 30 min, the rate of increase of the signal is very slow. As can be seen, the

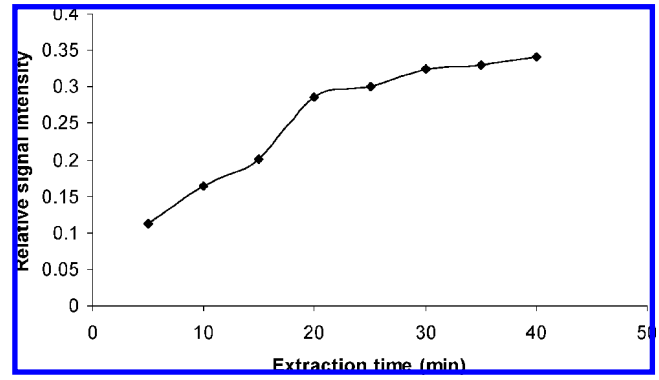


Figure 3. Effect of the extraction time on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C; APDC 0.05% (m/v).

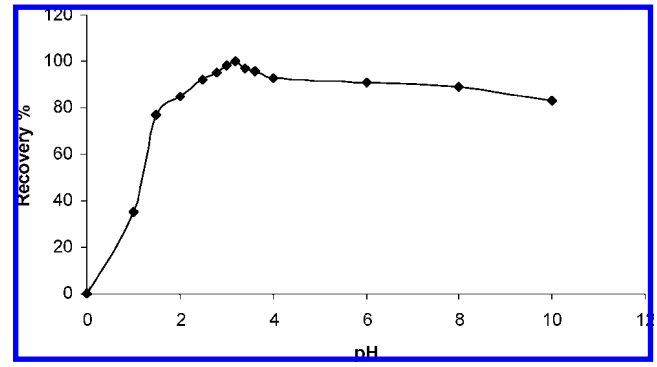


Figure 4. Effect of pH on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C; APDC 0.05% (m/v).

equilibrium state was reached after 30 min. An extraction time of 30 min was selected as a reasonable compromise between enrichment factor and analysis time.

Effect of pH. The next parameter evaluated on the determination of cadmium is the effect of pH. For this study, acetate, borate, and ammoniacal buffers at different pH values were used. The effect of pH was investigated within the range of 2.0−10.0. As seen in **Figure 4**, the best value of pH for maximum extraction efficiency was 3.2. As shown in **Figure 4**, the cadmium signal increased markedly with the increase of sample pH from 0 to 2.2, and then reached a plateau in the pH range of 2.2−10.0. Such a broad pH range provided convenience for the SME operation. Therefore, the sample pH was maintained at 3.2 with ammoniacal buffers in this study.

Temperature Effect. Temperature is a major parameter that can affect the extraction efficiency. This part of the work was carried out using a temperature range of 20−60 °C employing a thermostatted device. **Figure 5** clearly shows that the extraction efficiency increases as the solution temperature is enhanced till 35 °C. This is expected behavior since at higher temperature the mass transfer coefficients along with the rate constants are enhanced. However, at higher temperatures, the solubility of the organic drop in aqueous phase is increased and causes a reduction in organic extraction volume, and the dispersion of the microdrop is increased too. Therefore, an extraction temperature of 35 °C was selected for this work.

Ionic Strength. The influence of salt addition on the efficiency of SME was also investigated. Usually, the presence of salt increases the ionic strength of aqueous solution and would affect the solubility of the cadmium complex. This can be explained by the engagement of water molecules in the hydration spheres around the ionic salt. These hydration spheres reduce

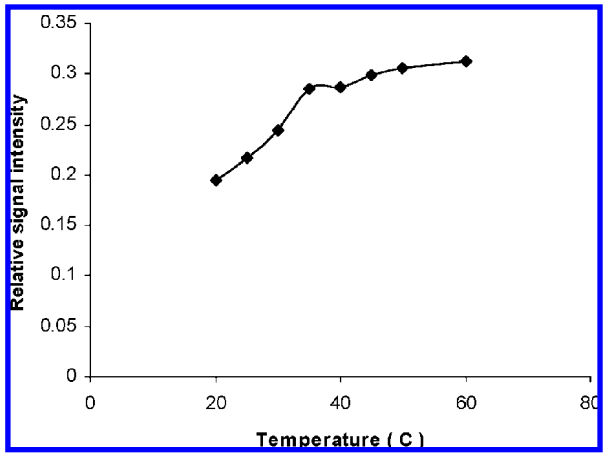


Figure 5. Effect of temperature on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C; APDC 0.05% (m/v).

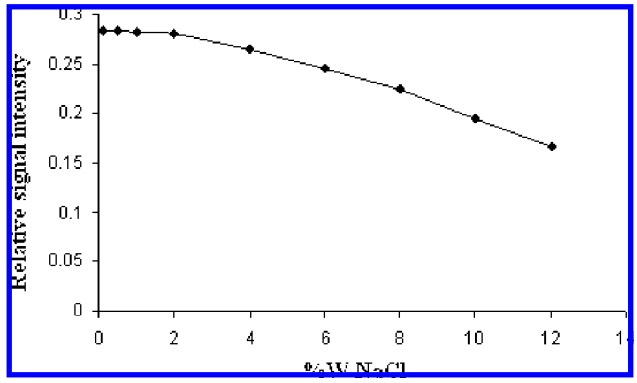


Figure 6. Effect of ionic strength on SME−preconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C; APDC 0.05% (m/v).

the concentration of water available to dissolve solute molecules. This should, then, drive additional solutes into a nonpolar sorbent or extractant. This effect is rather important for SPME, and addition of more than 1% of sodium chloride to enhance the extraction efficiency of the fibers has been reported (*17*−*19*). The addition of salt might change the Nernst diffusion film physical properties, and it reduces the diffusion rates of solutes into the micro drop and consequently lowers the analytical signals (**Figure 6**).

Effect of APDC Concentration. The effect of concentration of the chelating reagent (APDC) on the analytical signal was studied in this section. Under the optimum pH, the effect of the APDC concentration as a chelating agent on the analytical signal was studied; the results are shown in **Figure 7**. Also **Figure 7** indicates the extraction is completed at the concentration of 0.05% (m/v) APDC. A concentration of 0.05% (m/v) was chosen as the optimum concentration for the subsequent experiments. A solution containing 10% HNO_3 (v/v) and 20% methanol (v/v) was added to dilute the organic phase to 600 μL scale to reduce its viscosity before FAAS determination.

Figures of Merit. The calibration standard series for Cd was prepared by different Cd standard solutions being subjected to the SME procedure. The working range of the calibration curve was from 0.05 to 7.0 mgL^{-1} for Cd. The calibration function was $A = 0.0071 + 0.3541C$ with a correlation coefficient 0.9935, where A was the integrated absorbance, and C was the concentration of Cd (μgL^{-1}). The detection limit calculated according to three times the standard deviation of the blank signal and was found 0.8 ngL^{-1}. The reproducibility of the

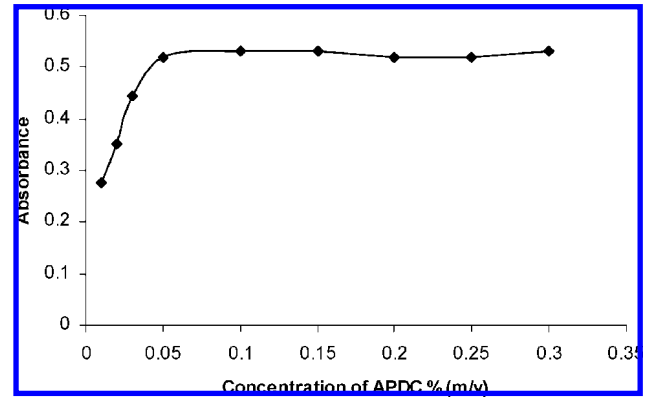


Figure 7. Effect of APDC concentration on SME−peconcentration performance: Cd (20 μgL^{-1}); pH 3.2; 1-octanol as extractor solvent; temperature of 35 °C.

Table 1. Analytical Characteristic Data of the SME−FAAS

parameter	SME−FAAS
calibration function (C in μg/L)	$A = 0.0071 + 0.3541C$
correlation coefficient (R)	0.9935
limit of detection (ng/L)	0.8
enrichment factor	93
upper linear range (mg/L)	0.05−7.0
precision (RSD, $n = 11$)	2.2%

Table 2. Effect of Foreign Ions on the Preconcentration and Determination of Cd (60 ng mL^{-1}) Ions

ions	concentration (mgL^{-1})	recovery %
Na^+	2.5×10^4	100.1
K^+	4×10^3	99.7
Ca^{2+}	120	101.4
Mg^{2+}	70	100.7
Ag^+	50	99.3
Al^{3+}	40	101.5
Fe^{3+}	80	99.6
Co^{2+}	100	99.1
Ni^{2+}	10	100.2
Zn^{2+}	20	100.5
Cu^{2+}	25	99.5
Mn^{2+}	5	99.5
Hg^{2+}	100	99.2
Ba^{2+}	100	101.4
Pb^{2+}	35	99.8
Cr^{3+}	2	101.5

method was studied for five replicate determinations of Cd in an aqueous sample spiked with 0.2 μgL^{-1} of Cd after extraction by APDC−octanol solutions. The preconcentration factors calculated as the ratio of the concentration of the analyte after preconcentration to that before preconcentration, which gives the same absorbance peak area, was 93 for Cd. The relative standard deviation (RSD) was 2.2% (see **Table 1**).

Interferences Effects. In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. The results indicated that the Cd recoveries are almost quantitative in the presence of interfering cations (**Table 2**).

Analysis of Meat and Fish Samples. The proposed SME−FAAS methodology was applied to the determination of cadmium in several meat samples. The meat and fish samples were collected from the north of Iran and were analyzed by SME combined with FAAS for the determination of cadmium. The concentrations of cadmium in the difference meat and fish samples are shown in **Table 3**. These samples were spiked with

Table 3. Determination of Cd in Meat and Fish Samples and Relative Recovery of Spiked Cd in Meat and Fish Samples

sample	conc. of Cd^{2+} (ppm)	added Cd^{2+}(ppm)	found Cd^{2+} (ppm) mean S.D.[a]	relative recovery (%)
meat # 1	8.3 ± 0.2	5.0	13.7 ± 0.2	103
meat # 1	7.1 ± 0.3	5.0	11.5 ± 0.4	95
fish #1	12.6 ± 0.2	5.0	15.3 ± 0.3	87
fish #1	13.5 ± 0.3	5.0	17.4 ± 0.3	94

[a] Standard deviation ($n = 3$).

cadmium standards to assess matrix effects. The relative recoveries of cadmium from these samples were 103, 95, 87, and 94%, respectively (**Table 3**). These results demonstrated that the meat and fish sample matrices, in our present context, had little effect on the SME of cadmium. It is clear from the above discussion that SME was combined with FAAS for the determination of cadmium in meat and fish samples. This method is very simple, sensitive, and inexpensive. The method was based upon direct contact of the extracting microdrop with the sample solution. Influential parameters such as the type of solvent, extraction time, stirring rate, temperature, and ionic strength were optimized.

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Received for review September 2, 2008. Revised manuscript received November 19, 2008. Accepted November 21, 2008. This work was supported by a research grant from Shahrood University of Technology.

JF8027057